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and
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of
GAS CHROMATOGRAPHY

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PREFACE

The phenomenal growth of interest in gas chromatography is reflected in many ways. Three-fourths of the papers in the literature have appeared in the last three years. At least fifteen companies in the United States alone now produce commercial instruments, nearly all of which have been developed in the last three years. The fields of application are increasing as fast as they can be counted. Confronted with this exponential expansion, the average chemist can no longer keep up with developments, indeed he may find it difficult to know where to begin.

In response to many requests, the University of California, Los Angeles, offered a first course in gas chromatography February 2-6, 1959. The lecturers were asked to summarize the material then available. Each lecture covered a particular phase (including "stationary" and "mobile") of gas chromatography. In effect, we attempted to chromatograph all of the information and ideas available, and then tried to isolate and expand those topics of most value to beginners and to those with limited experience.

This book is an outgrowth of the course. The lectures have been organized, elaborated, and edited to provide continuity and consistency. Gas chromatography is controlled by a veritable maze of variables, few of which can readily be isolated for independent discussion. Thus, some duplication of material is inevitable. Wherever repetition was con-

sidered to be helpful to the reader, we have let it stand.

As in most fields of analytical chemistry, an appreciation of the basic principles is essential to the development of applications and the intelligent interpretation of the results. Therefore, the first part of this book is concerned with a discussion of theoretical principles underlying partition chromatography and a description of the mechanism of separation when the mobile phase is an inert gas. In deference to the reader who may be more interested in "how to do it", we have omitted long mathematical treatments. These chapters are followed by a more detailed description of the mobile and stationary phases. The practical details and general procedures are described in the chapters covering the effects of operational parameters, column selection and construction, sample introduction, and temperature control. General methods available for converting the experimental data into useful results are discussed in the final chapter on analytical methods.

We have not intended to review critically a large number of applications. To do this properly would require a volume several times larger than the present work. As a partial substitute, titles of all papers have been included in the extensive bibliography which is essentially complete through 1958 - plus some early 1959 references. Only a few papers in relatively inaccessible journals and papers presented at local meetings have been omitted. The list was compiled from a number of sources starting from a bibliography kindly furnished to the editor by Beckman Instruments, Inc.

Much of the material in Chapter 13 was originally prepared by Hadley Ford of the Stanford Research Institute. We wish to thank him for his cooperation. In order to make the book available before much of the material becomes superceded by newer techniques and apparatus, we have decided to reproduce the text by the photo offset method. We are greatly indebted to our typist, Nancy Hinchliff, who is responsible for the exacting preparation of the final copy.

Los Angeles, California Robert L. Pecsok
April 1959

SYMBOLS AND TERMS

Page numbers on which symbols are used follow each definition.

A	coefficient of eddy term in simplified van Deemter equation: 13, 44, 57
A	peak area, sq. cm: 124
$\underline{a}$	modified activity coefficient: 21, 63
$\underline{a}$	area of cross section of column occupied by gas phase: 30
B	coefficient of diffusion term in simplified van Deemter equation: 13, 44, 57
B	constant: 31
C	constant: 31
C	coefficient of mass transfer term in simplified van Deemter equation: 13, 44, 57
C_1	chart speed, cm/min: 42

SYMBOLS

C_1 recorder sensitivity, mv/cm: 124

C_2 detector amplification factor: 42

C_2 chart speed, min/cm: 124

C_3 carrier gas flow rate: 42, 124

D_{gas} diffusion coefficient of solute in gas phase: 13, 57

D_{liq} diffusion coefficient of solute in liquid phase: 13, 57

$\underline{d}_f$ average thickness of liquid film: 13, 57

$\underline{d}_p$ average particle diameter: 13, 57

F_c volume rate of flow of carrier gas: 30, 46

g proportionality constant: 42

H partition coefficient, the amount of solute per unit volume of liquid phase divided by amount of solute per unit volume of gas phase: 25

H_a equilibrium constant for adsorption: 30

HETP height equivalent to a theoretical plate: 12, 13, 44, 57

$\underline{k}'$ fraction of sample in liquid phase divided by fraction of sample in gas phase: 13, 57

$\underline{l}$ length of column: 30

$\underline{m}$ weight of sample component: 42

$\underline{m}_i$ moles of solute $\underline{i}$: 19

$\underline{n}$ total number of plates: 12, 18, 44, 56

$\underline{n}_a$ moles of component adsorbed: 29

$\underline{n}_g$	moles of component in gas phase: 29
P.I.	performance index: 19
P^o	vapor pressure of pure solute: 21
$\overline{p}$	average column pressure: 47
p_i	column pressure at inlet: 46
p_o	column pressure at outlet: 46
Q_a	heat of adsorption: 30
Q_s	heat of solution: 31
Q_v	heat of vaporization: 31
R	gas constant: 30
r	recorder response, peak area: 42
S	sensitivity parameter: 124
s	detector sensitivity, mv/weight of solute: 42
T	absolute temperature: 30
$\underline{t}$	retention time of component (Golay): 19
$\underline{t}_a$	retention time of air: 19
$\underline{t}_R$	retention time: 12, 30, 43, 46
$\underline{u}$	linear gas velocity: 13, 44, 57
$\underline{u}$	average linear velocity of solute zone: 29
$\underline{u}_g$	linear velocity of carrier gas: 29
V_G^o	interstitial volume of column: 30

SYMBOLS

V_g specific retention volume = 273 H/T ρ_L: 26

V_L volume of liquid phase in column: 31

V_R retention volume: 47, 56

V_R^o limiting (corrected) retention volume with zero pressure drop: 47

W weight of component, mg: 124

α relative volatility: 21

α separation factor: 18

γ activity coefficient: 24, 65

γ correction factor for tortuosity of interparticle spaces: 13, 57

ΔH_v heat of vaporization: 37

$\Delta \underline{p}$ pressure drop across column: 19

$\Delta \underline{t}$ peak width at base: 12, 44

$\Delta \underline{t}$ peak width at half height (Golay): 19

ΔV peak width at base: 56

η^- fractional band impurity: 18

λ measure of packing irregularity: 13, 57

ρ_L density of liquid phase: viii

σ standard deviation: 129

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Chapter 1

INTRODUCTION

H.W. Patton

Tennessee Eastman Company

THE MOST RECENT MEMBER of the chromatography family has a very remarkable record. It was conceived more than ten years before birth, and within seven years, it has become a tremendous giant that seems to be growing at an ever increasing rate. With proper qualification and interpretation, the sentences above describe the history of gas-liquid chromatography. The principles of this method were clearly described by Martin and Synge in 1941 in a paper devoted primarily to the introduction of another kind of chromatography (5). The idea of using a gaseous moving phase, which later proved to be so valuable, was apparently not exploited until James and Martin published their classical paper in 1952 (44).

Historical Background. Chromatographic methods can be subdivided according to the physical nature of the phases and to the separation mechanism involved. As a background for the discussion of gas chromatography, a tabulation of various kinds of chromatography is given in Table 1-1.

Although several workers preceded Tswett with methods that might be called chromatography, he is generally given credit for inventing the method (140). He obtained some separations that were quite remarkable at the time (1903). For example, he separated the extract of green

TABLE 1-1 CHROMATOGRAPHIC METHODS

Liquid Phase Column Chromatography	
Adsorption	Tswett, 1903
Partition	Martin and Synge, 1941
Ion-Exchange	Various Workers, 1947
Paper Chromatography	Consden, Gordon and Martin, 1944
Gas Chromatography	
Adsorption	Hesse, 1942
Partition	James and Martin, 1952

leaves into several components by pouring the solution onto one end of a column of adsorbent and then passing fresh solvent through the column. The material initially forming a green band at the top of the column was caused to move down the column and form several bands having various shades of green and yellow. Because his separations involved colored materials, Tswett called the process "chromatography". The term "chromatography" as used today is generally a misnomer, but it is well established and it is unlikely that it will be replaced by a more descriptive name.

In spite of the simplicity and power of Tswett's methods, they were used very little until 1931 when Kuhn and Lederer used chromatography to separate α - and β - carotene. The results of this work were soon well known and highly regarded. Many workers in several countries experimented with chromatographic methods, and the field developed rapidly.

DESCRIPTION OF METHODS

It is difficult to devise a simple definition of chromatography that includes all chromatographic processes and excludes other separatory processes. Perhaps it is sufficient to outline some of the features of common chromatographic methods.

All chromatographic methods involve distribution of the material to be separated between two phases which

move with respect to each other. Generally one phase is fixed and the other is mobile. The fixed phase must be solid or liquid, otherwise it cannot be conveniently held fixed. The mobile phase can be either a liquid or a gas. Thus, there are four kinds of chromatography according to the kinds of fixed and mobile phases used.

Any chromatographic method that uses a gaseous mobile phase is called gas chromatography. The nature of the fixed phase is the basis for two major subdivisions. If the fixed phase is a solid, such as activated charcoal, the method is called gas-solid chromatography (abbreviated GSC). The term gas-liquid chromatography (GLC) or gas-liquid partition chromatography, applies when the fixed phase is a liquid. Generally the fixed liquid is used as a thin film on solid particles or on the inner wall of a capillary column.

Gas chromatographic methods can also be classified according to the means of moving the sample through the column. Elution, displacement and frontal analysis are the most commonly employed methods. All three methods can be used with adsorption columns (GSC), but only elution is applicable to partition columns (GLC).

Frontal Analysis. During a frontal analysis, the mixture to be analyzed (suitably diluted in a carrier gas in some cases) is passed continuously through a column of adsorbent. The components emerge from the column in the order of their relative affinities for the adsorbent, but only the first one is separated from all other sample components. Ideally, a plot of concentration versus time for sample components in the column effluent is like that shown in Fig. 1-1. Of course, an indiscriminate detector such as a thermal conductivity cell records only the heavy profile line and does not indicate the concentrations of individual components. Because of displacement effects, the concentration of a given component in the effluent usually decreases as other components appear.

Interpretation of the experimental curve for the purpose of identification and determination of the components present is possible but rather complicated compared to displacement or elution.

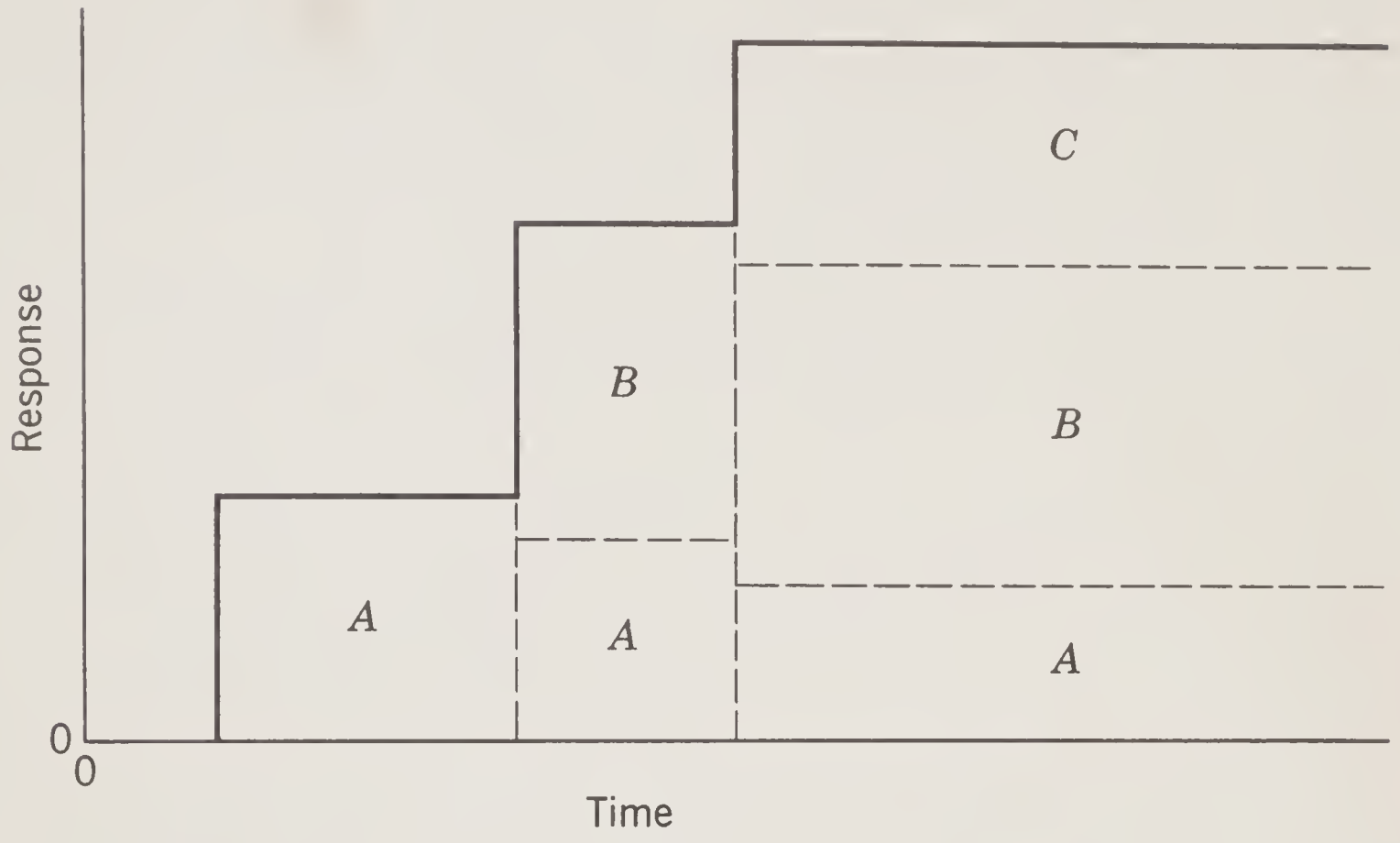

Fig. 1-1. Chromatogram for ideal frontal analysis.

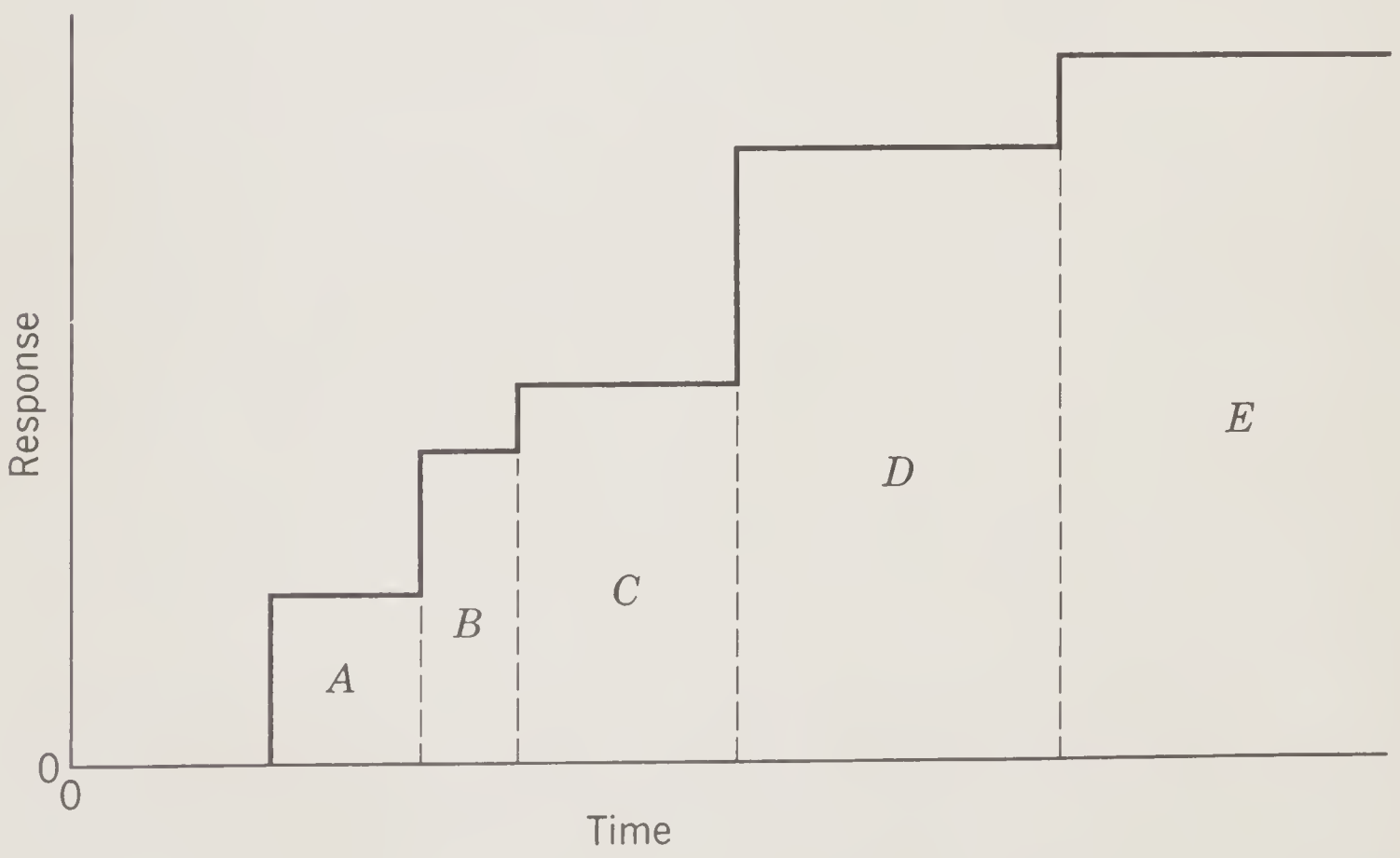

Fig. 1-2. Chromatogram for ideal displacement analysis.

Displacement Analysis. The essential features of displacement analysis are as follows. The sample is put on one end of a column of adsorbent. A carrier gas containing the vapor of a substance more strongly adsorbed than any sample component is passed through the column. This substance displaces the sample from the adsorbent and each sample component in turn displaces others that are less strongly adsorbed. The components arrange themselves in well defined zones in order of increasing affinity for the adsorbent and eventually move to the end of the column where they emerge in succession. A plot of concentration versus time for an ideal displacement analysis is shown in Fig. 1-2. The height of a given step is the means of qualitative identification. The length of the step is proportional to the amount of material that produced it, with a different proportionality constant for each substance.

Of course, there is always a region between adjacent components that contains a mixture of the two. However, it is generally possible to arrange experimental parameters so that the amount of material in this region of mixing is a small portion of the total.

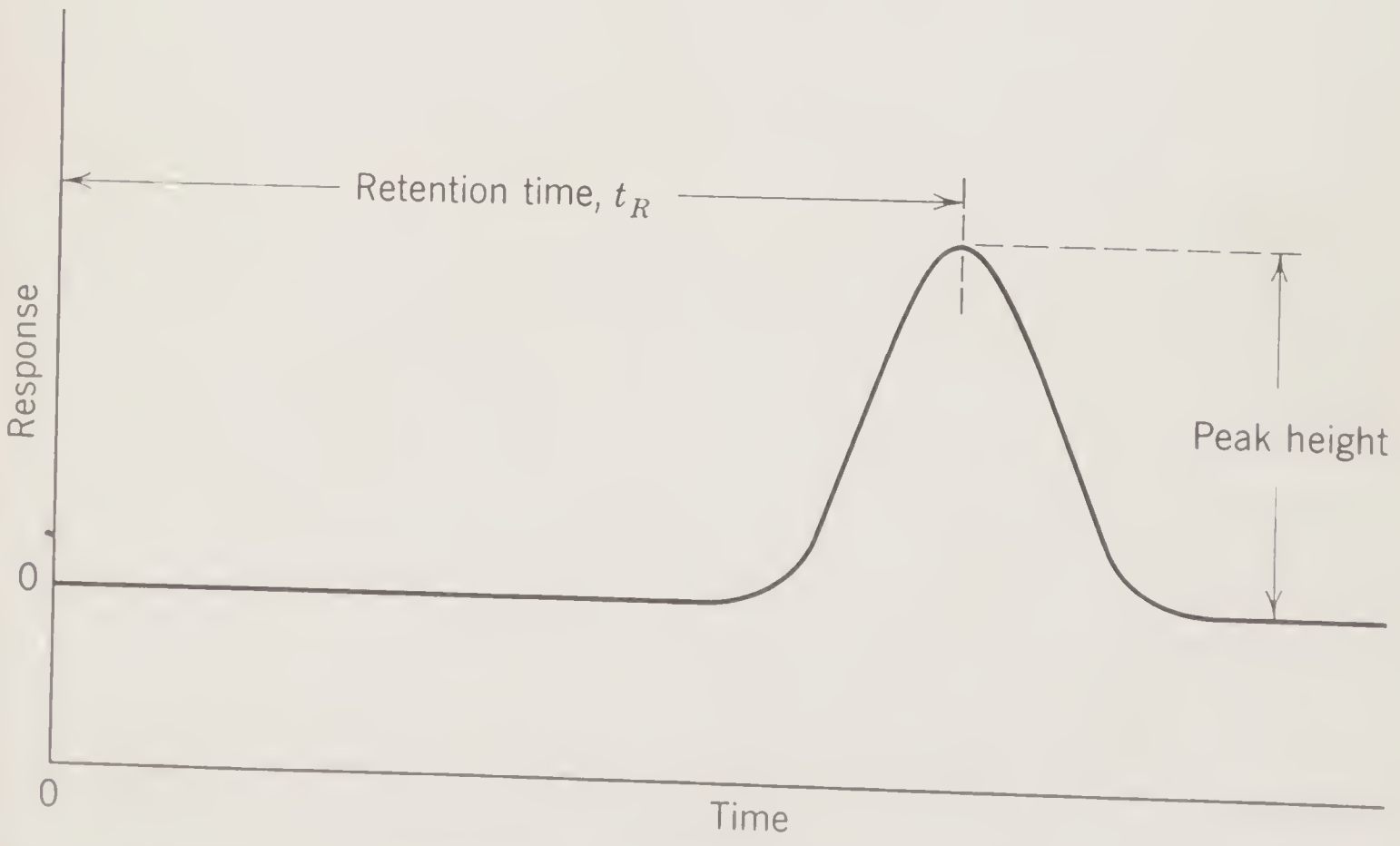

Fig. 1-3. Chromatogram for ideal elution of one component.

Elution. Elution involves passing a carrier gas continuously through the chromatographic system. A gaseous or volatile liquid sample is introduced into this gas stream and carried onto the column of adsorbent. Each sample component distributes itself in a characteristic manner between the gaseous phase and the fixed phase (solid or liquid), and that portion in the gaseous phase moves with the carrier

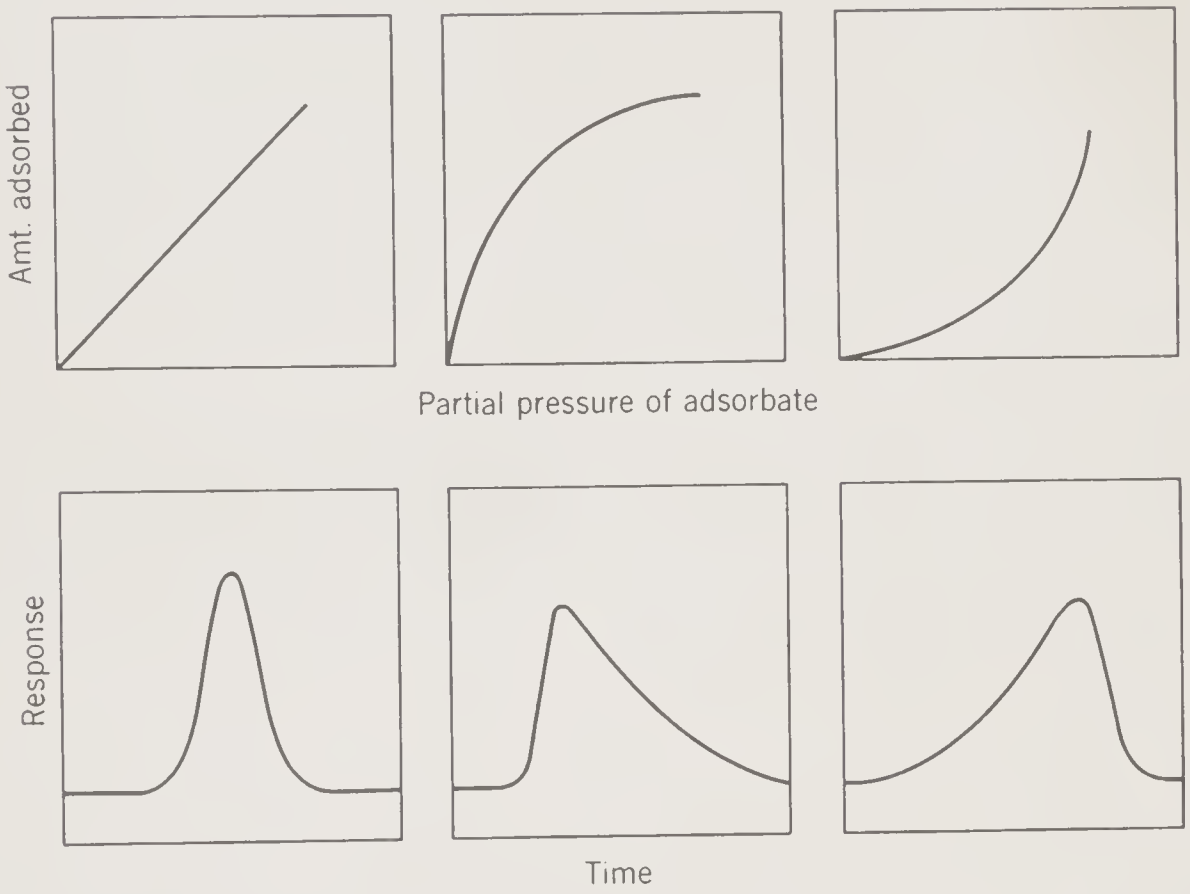

Fig. 1-4. Typical isotherms and corresponding chromatographic peaks.

stream. In favorable cases the sample components are separated and pass from the column in the effluent stream at different times. Fig. 1-3 shows an ideal elution curve for one component. The retention time is the means of qualitative identification and the height of the peak or the area under it is proportional to the amount of the substance that produced it. Ideally, a separate peak is produced for each component in the sample mixture, and there is negligible overlap of adjacent components.

Unless there is distortion due to instrumental or operational factors, the shape of the elution peak for a component is related to its adsorption (or solution) isotherm. Three common types of isotherms and the corresponding

elution peaks are shown in Fig. 1-4. The symmetrical peak which is associated with a linear isotherm is the most desirable for analytical purposes. Some asymmetry can be tolerated, but if it is excessive, the components move in overlapping zones of low concentration.

Unfortunately, for the purposes of gas-solid elution chromatography, isotherms for the adsorption of most substances are not linear but resemble the center example of Fig. 1-4. Consequently, elution from adsorbents generally results in peaks with sharp "fronts" and long "tails". Nevertheless, elution from adsorbents produces usable chromatograms in many cases, and there are a few examples of adsorbents that produce highly symmetrical peaks (657).

Symmetrical or nearly symmetrical elution peaks are rather common in gas-liquid chromatography. Non-ideal solutions can, however, result in asymmetry of either the "tailing" (Fig. 1-4, center) or "leading" type (Fig. 1-4, right). In gas-liquid systems, adsorption of the sample components by the solid material supporting the fixed liquid sometimes occurs to such an extent that severe tailing results. Peak distortions are discussed in more detail in Chapter 7.

Chapter 2

FUNDAMENTAL PRINCIPLES

H. W. Patton

Tennessee Eastman Company

GAS-LIQUID METHODS are undoubtedly applicable to a wider variety of problems than are adsorption methods. This fact is due in part to the sharp symmetrical peaks usually produced and also to the tremendous variety of liquids that can be used to obtain the desired selectivity. Because of the much greater importance of gas-liquid methods in practice, some time will be spent discussing the mechanism of separation on this type of column, and some of the factors affecting the efficiency of separation will be considered. A part of what will be said is also applicable to adsorption columns with elution development.

PARTITION CHROMATOGRAPHY

If a gas-liquid column is visualized as operating in a manner somewhat analogous to a distillation column, a theoretical plate treatment like that first described by Martin and Synge (5) is applicable. A theoretical plate is defined as a section of the column in which the vapor leaving the section has the composition that would be in equilibrium with the average concentration of liquid solution within the section. In the process of passing through one theoretical plate the equivalent of one equilibration between the liquid phase and vapor phase occurs.

The over-all separation achieved with a column depends on two things - separation per plate (separation factor) and the number of plates. The separation produced by one equilibration is determined primarily by the nature of the high-boiling liquid, the nature of the components to be separated, and the temperature. The number of theoretical plates in a column of given dimensions depends in a rather complicated way on many factors, for example, rates of diffusion in the two phases, thickness of liquid layer, uniformity of column packing, nature of carrier gas, and flow rate of carrier gas. The number of effective theoretical plates is increased by an increase in column length, within limits, and decreased slightly by an increase in column diameter.

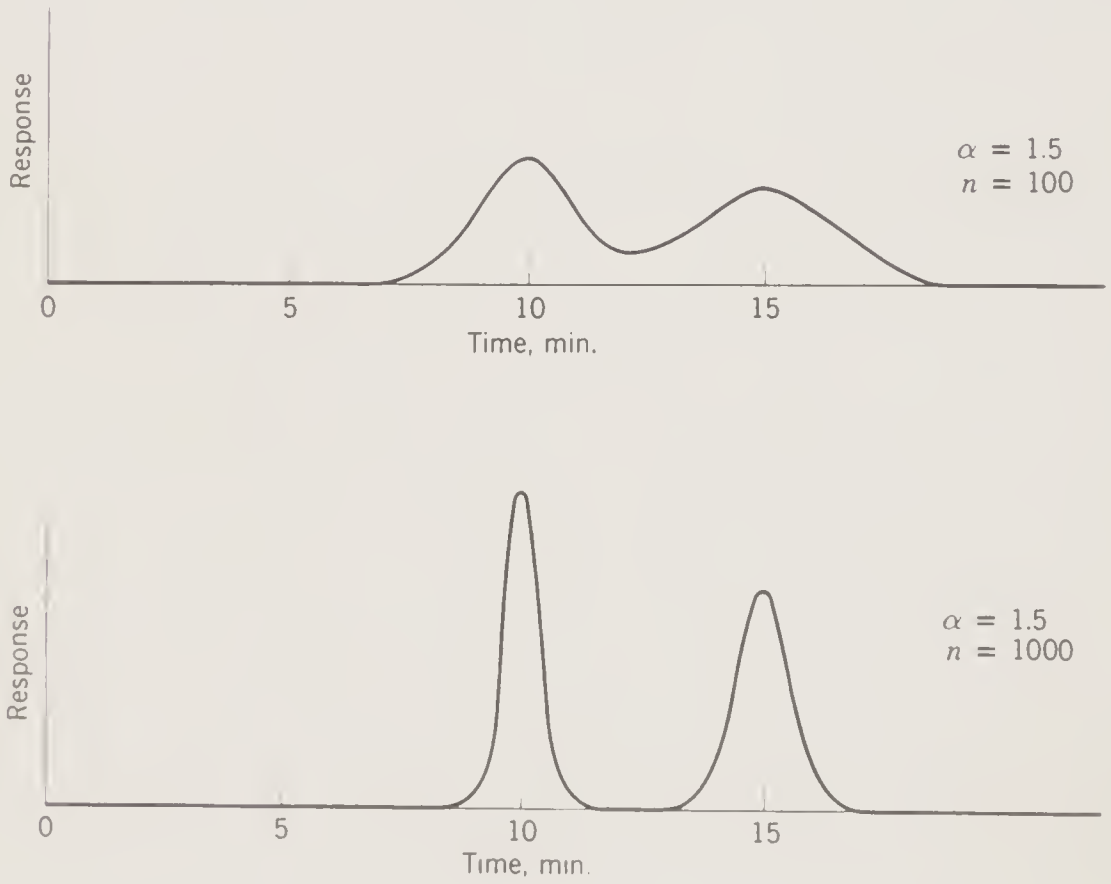

Fig. 2-1. Hypothetical chromatogram illustrating effect of separation factor and number of theoretical plates on degree of separation.

In terms of a chromatogram of two components the separation factor is equal to the ratio of the two retention times. The sharpness of the peaks is a measure of the number of theoretical plates. For example, Fig. 2-1 shows two hypothetical chromatograms, for each of which the separation factor is 1.5. However, the separation is greatly im-

proved in the lower example because of the greater number of theoretical plates. In principle, the separation of two substances can be improved either by using a column liquid with better selectivity (larger separation factor) or by operating the column so as to increase the number of theoretical plates. In practice, the selectivity of the column liquid can be used to advantage except when the substances to be separated are very similar. Of course, it is generally desirable to operate with as many theoretical plates as possible, consistent with other requirements.

Selectivity of the Column Liquid. Final choice of a column liquid with suitable selectivity for a given separation is generally based on actual chromatographic experiments with materials considered to be good prospects. Although separation factors can be evaluated from static distribution studies, it is generally easier to prepare a column and to test its chromatographic behavior than to evaluate it by other means. However, even crude knowledge of intermolecular interactions is a help in choosing the substances to be tested. To illustrate qualitatively the sort of effects that are encountered, some examples will be given.

When a mixture of benzene and cyclohexane are put through a column in which the column liquid is hexadecane or paraffin oil, the benzene precedes the cyclohexane. If, under the same conditions, a column containing tricresyl phosphate or benzylbiphenyl is used, the cyclohexane precedes the benzene. Generally, column liquids containing aromatic rings selectively detain aromatic compounds.

Polar liquids interact preferentially with polar sample components. The retardation of polar vapors is particularly important when hydrogen bonding is involved. For example, water and alcohols are selectively detained on columns containing glycerol or ethylene glycol.

Specific interactions leading to weak complex formation sometimes cause excellent selectivity. For example, ethylene glycol saturated with silver nitrate can be used to separate alkenes and dienes from the corresponding alkanes. The unsaturated compounds are also separated from one another in many cases because of their different degrees of interaction with the silver ions. Alkynes interact very strongly with the silver ions probably forming acetylides

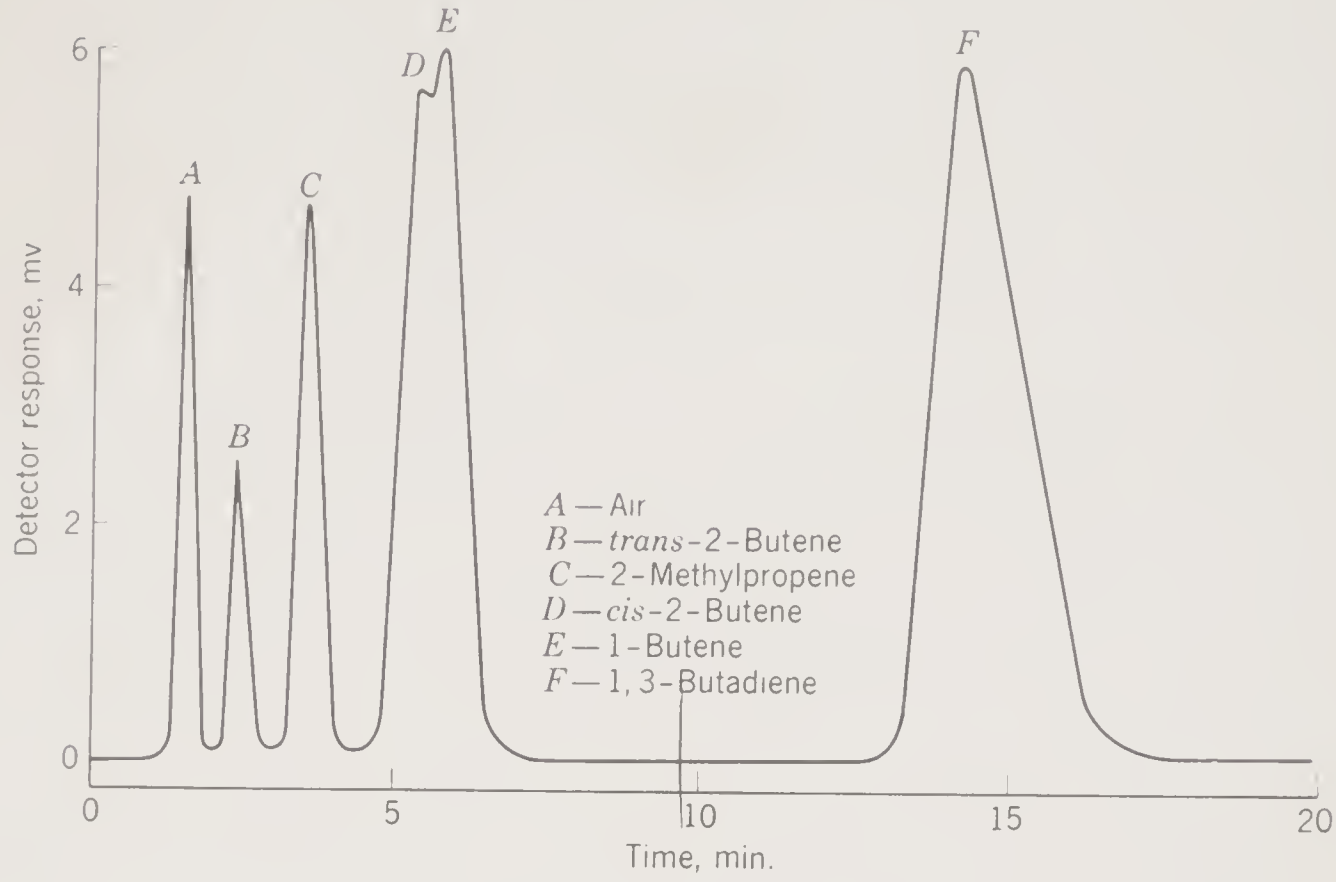

Fig. 2-2. Chromatogram of C_4 hydrocarbons using a column containing ethylene glycol saturated with silver nitrate.

which remain on the column. The elution curve for a sample of hydrocarbons from a silver nitrate-ethylene glycol column at room temperature is shown in Fig. 2-2.

Even with such similar substances as meta- and para-xylene, the separation factor can be varied somewhat by using different column liquids (673). The subtle solvent-solute interactions responsible for this behavior are not understood.

THEORETICAL PLATE TREATMENT

The number of theoretical plates can be calculated from several expressions which do not necessarily give the same results. However, each is essentially a measure of the peak sharpness, and all give about the same relative values. The carrier gas can be considered to move intermittently from plate to plate, as in the original treatment of Martin and Synge (5), or continuously as assumed by Glueckauf (117). The relative peak width can be evaluated in several ways (5, 143, 698). The method of calculation

commonly accepted is shown in Fig. 2-3. The number of plates, n, is given in terms of the retention time measured from the introduction of the sample, t_R, and the peak base measured at the points where the extended tangents intersect the base line, Δt.

$$n = 16 \left(\frac{t_R}{\Delta t} \right)^2 \qquad (2\text{-}1)$$

The units used in equation 2-1 can be either time or volume

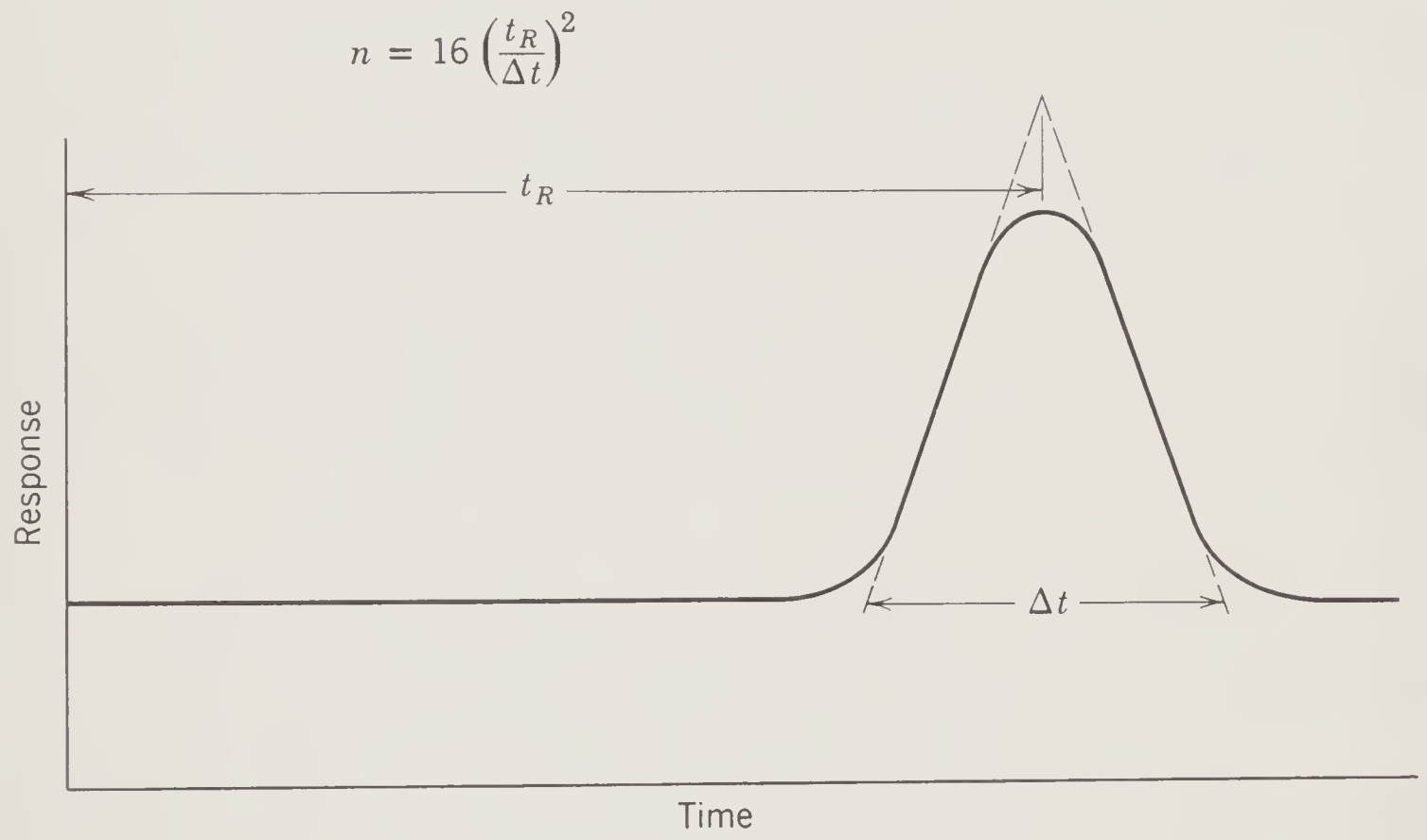

Fig. 2-3. Recommended method for calculating number of theoretical plates.

as long as they are consistent. The height equivalent to a theoretical plate (HETP) is obtained by dividing the column length by the number of plates. It is worthwhile to note that HETP, which one might naively assume to be independent of retention time, generally decreases with increasing retention time. However, HETP may increase with increasing column length. Low values of HETP correspond to efficient column operation.

The plate theory provides a very useful means of evaluating column efficiency, but it does not help the experimenter decide how to operate his column so as to obtain best efficiency. The so-called rate theory of van Deemter is a very useful basis for considering the effects of several column and operational parameters (316). The van Deemter equation in its complete and simplified forms is shown below.

$$HETP = 2\lambda \underline{d_p} + \frac{2\gamma D_{gas}}{\underline{u}} + \frac{8\ \underline{k'}}{\pi^2(1+\underline{k'})^2}\ \frac{\underline{d_f}^2}{D_{liq}}\ \underline{u} \qquad (2\text{-}2)$$

$$HETP = A + B/\underline{u} + C\underline{u} \qquad (2\text{-}3)$$

Eddy Diffusion	Molecular Diffusion	Resistance to Mass Transfer

The HETP is, of course, the height equivalent to a theoretical plate, and it is almost invariably computed from equation 2-1. Other symbols in the equation are: λ, a quantity characteristic of the packing; $\underline{d_p}$, average particle diameter; γ, a correction factor for the tortuosity of the interparticle spaces; D_{gas}, diffusion coefficient in the gas phase; $\underline{u}$, linear gas velocity; $\underline{k'}$, fraction of sample in liquid phase divided by the fraction in the vapor phase; $\underline{d_f}$, thickness of liquid film; and D_{liq}, diffusion coefficient in liquid phase.

The van Deemter theory is concerned with the influences which tend to broaden chromatographic bands as they move down the column. According to the theory there are three such factors which are called eddy diffusion, molecular diffusion, and resistance to mass transfer. The eddy diffusion contribution results from the irregular paths the gas takes through the packed column. These paths have different lengths, cross sections, and directions. As a result of these irregularities the chromatographic band is spread along the column. The two factors, other than the numerical constant in the eddy diffusion term are $\underline{d_p}$, the average particle diameter, and λ, a quantity characteristic of the packing. Reducing the particle size should decrease the eddy diffusion contribution to HETP. Uniformity of particle size and proper packing help to reduce λ.

Molecular diffusion of the sample molecules in the carrier gas is the second cause of band broadening. The

contribution to HETP from this factor increases with decreasing molecular weight of the carrier gas. Thus nitrogen, argon and carbon dioxide are preferable to hydrogen and helium with regard to column efficiency. Diffusion decreases with increasing pressure of the carrier gas. Increasing temperature increases diffusion.

The term designated resistance to mass transfer involves several parameters. $\underline{k}'$ is the ratio of the amount of sample dissolved in the liquid phase to that in the gaseous phase. Its value depends on the partition coefficient and the relative volumes occupied by liquid and gas in the column. Generally $\underline{k}'$ is greater than one, and under this circumstance increasing $\underline{k}'$ reduces HETP. Thus it is expected that components with greater solubility in the liquid phase will lead to somewhat smaller HETP.

The effective thickness of the liquid film, $\underline{d_f}$, appears to the second power in the expression and, hence, would be expected to be an important factor. Reducing $\underline{d_f}$ increases column efficiency. However, if this result is achieved by decreasing the amount of liquid in the column, k' is decreased, thereby partially counteracting the improvement. Furthermore, with a porous support like kieselguhr, it is likely that beyond a certain limit, further reduction in the amount of liquid simply causes incomplete coverage of the surface rather than complete coverage by a thinner layer.

The liquid diffusion coefficient $D_{liq.}$ is affected by the viscosity of the column liquid. In some cases increased temperature may improve separations by decreasing the viscosity of the column liquid. Since other factors ($\underline{k}'$ and D_{gas}) are adversely affected, increased temperature may decrease column efficiency.

The factor in the van Deemter equation which has not been discussed yet is the flow rate of the carrier gas, $\underline{u}$. For discussion of the effect of flow rate it is convenient to consider the simplified form of the equation. It is apparent that eddy diffusion is independent of flow rate, the contribution to HETP from molecular diffusion is inversely proportional to flow rate, and resistance to mass transfer contributes in direct proportion to flow rate. From this relation it is expected that, if all other factors are constant, there will be an optimum flow rate for most efficient column operation. Fig. 2-4 shows the form of the relation graphi-

cally. At flow rates below the optimum, molecular diffusion makes a large contribution to HETP, and above the optimum, resistance to mass transfer is an important factor. For gases of high diffusivity, for example hydrogen and helium, the molecular diffusion contribution is particularly likely to be important. If the film of liquid is thick or of high viscosity, resistance to mass transfer may be dominant. Perhaps it is worthwhile to discuss one more point in connection with Fig. 2-4. Gases are compressible, and the pressure at the inlet end of a chromatographic column is greater than that at the outlet. It follows that the flow rate of carrier gas is always greater at the outlet end than at the inlet end. As a result, the column cannot operate at the optimum flow rate throughout its entire length. For columns of low pressure drop, this factor is of little importance. For columns containing very small particles of packing material, the pressure drop may be such that some parts of the column operate at very inefficient flow rates. Increasing the absolute pressure at both ends of the column decreases the ratio of inlet to outlet pressures and, hence, leads to a more uniform flow rate along the column. A correction factor is given in Chapter 4 for converting observed retention volumes

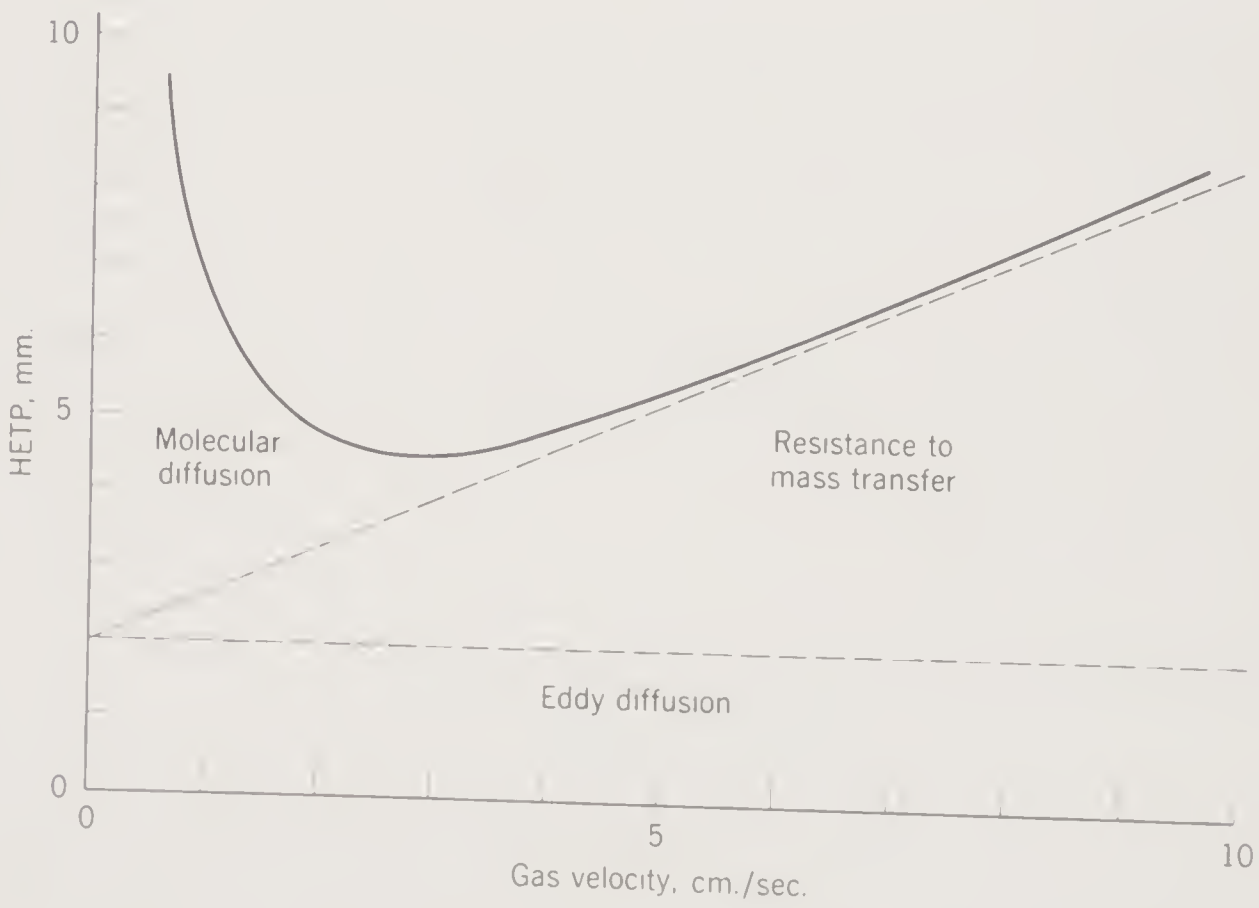

Fig. 2-4. Influence of carrier gas velocity on column efficiency.

to corrected volumes which are independent of the pressure.

There is a method, which has apparently not been used, to provide a constant linear velocity of carrier gas along the column. This result can be achieved, in principle, by varying the column diameter to compensate for pressure changes. An ideal column built on this principle would taper from the inlet to the outlet with a continuously increasing diameter. The ratio of the outlet diameter to the inlet diameter should equal the square root of the ratio of the inlet to outlet pressures. In practice, a column with this internal geometry would be difficult to fabricate. However, columns made of short sections of straight tubing with increasing diameters would approximate the desired geometry. If the ratio of inlet to outlet pressures can be reduced to less than two, the problem is no longer significant.

Qualitative expectation from the rate theory are summarized in Table 2-1.

TABLE 2-1. QUALITATIVE PREDICTIONS FROM RATE THEORY.

Change	Partial Effects	Effect on HETP
Particle Size		
Increase	Increase $\underline{d}_p$, decrease λ?	?
Narrow range	Decrease λ, γ	Decrease
Spherical	Decrease λ, γ	Decrease
Carrier Gas		
Increase density	Decrease D_{gas}	Decrease
Increase pressure	Decrease D_{gas}	Decrease
Increase flow rate		Minimum at optimum flow rate
Temperature		
Increase	Increase D_{gas}, D_{liq}, decrease $\underline{k}'$	?
Liquid		
Decrease amount	Decrease $\underline{k}'$, $\underline{d}_f$	Decrease
Decrease viscosity	Increase D_{liq}	Decrease

It is apparent that optimum separation of a sample is seldom achieved by simply packing a column with whatever is handy and operating it by rule-of-thumb. To find the optimum combination of all the variables involved by means of experiments designed for proper statistical analysis would be a considerable task. Evidently, no one has attempted so complete an analysis of any system. Fortunately, most analytical separations are achieved with little consideration for efficiency. Nevertheless, theory has been useful in cases where high efficiency was necessary, and also some improved rules-of-thumb have resulted from experimental work designed to test theory.

Experimental Tests of Rate Theory. Most of the studies conducted so far have been concerned with investigating the change in HETP as a result of changes in particle size and uniformity, ratio of liquid to solid, temperature, nature of the carrier gas and flow rate of carrier gas. In general, the van Deemter equation has been found consistent with experimental results. Bohemen and Purnell (540) have some indication that the eddy diffusion term is inversely proportional to flow rate rather than independent of flow rate. Other workers have generally found the form of the equation to be essentially correct.

Several recent papers have been devoted to investigation of the factors affecting column efficiency. There is general agreement that use of hydrogen or helium as carrier gas results in less efficient column operation than when nitrogen or argon is used. In spite of this fact hydrogen and helium are still widely used because they result in good sensitivity for thermal conductivity detectors.

Use of smaller particles of support material has been found to give better efficiency in practice. It is particularly important to use particles of uniform size. There is rather general agreement that column efficiency increases with decreasing ratio of high-boiling liquid to solid support. There is evidently a limit below which adsorption becomes important, but several workers have found increasing efficiency with amounts of liquid down to about 2%. With "lean" columns only extremely small samples can be used. Column efficiency increases with decreasing sample size.

The use of higher than atmospheric pressure in a chromatographic column improves efficiency for two reasons. First, molecular diffusion is reduced because of increased density of the carrier gas. Second, at a given pressure drop across the column, the flow rate of carrier gas is more uniform (640). Further tests of the rate theory are described in Chapter 6.

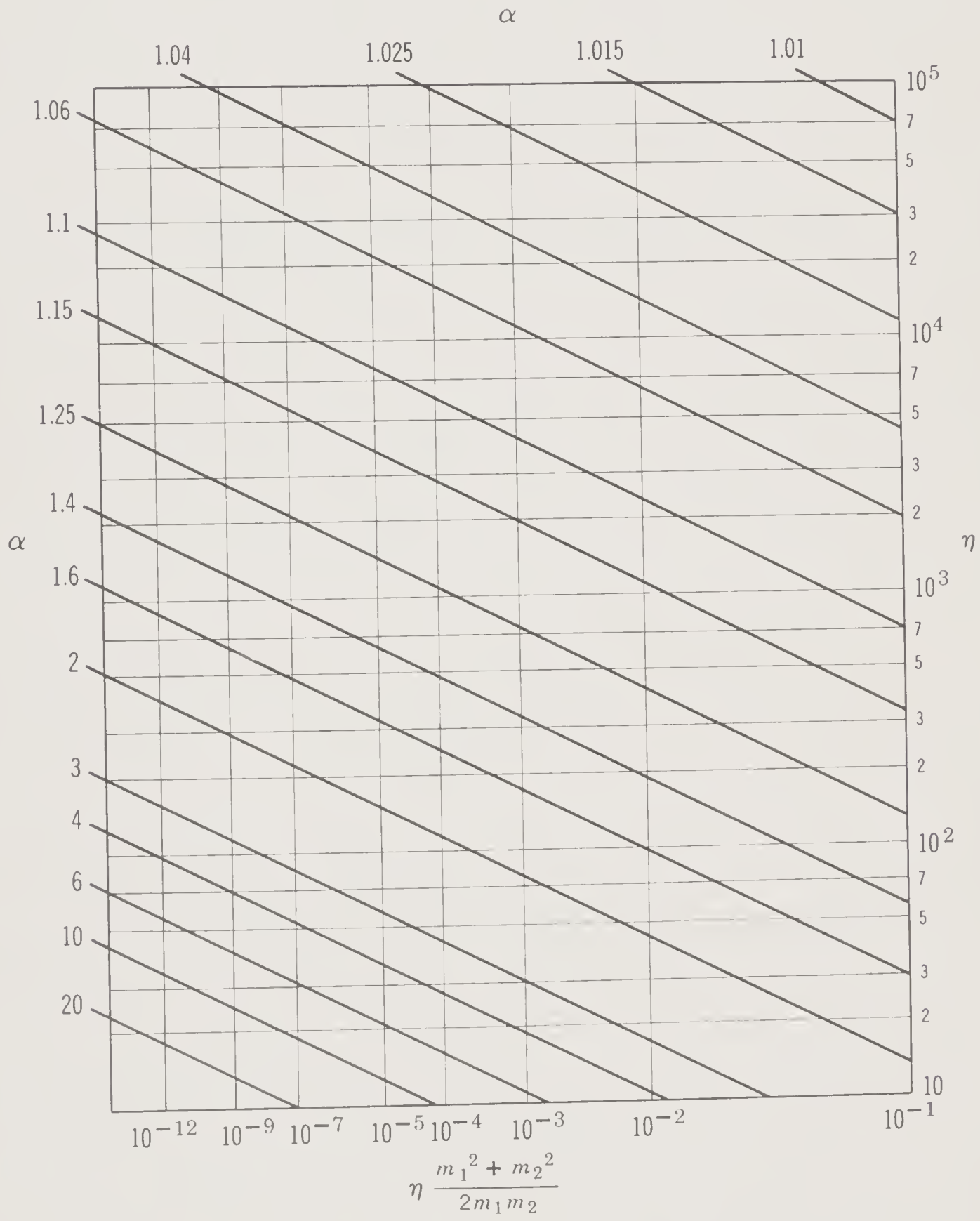

Fig. 2-5. Number of theoretical plates (n) and separation factor (α) required to give fractional band impurity (η). After Glueckauf (117).

The relation among separation factor, number of theoretical plates, and degree of separation has been worked out by Glueckauf (117). The results can be presented in the form of a very useful graph like that shown in Fig. 2-5. The number of theoretical plates $\underline{n}$ is plotted versus the factor $\eta\,(m_1^2+m_2^2)/\,2m_1\,m_2$ where η is the fractional impurity in each separated fraction and m_1 and m_2 are the respective numbers of moles of the two substances in the mixture to be separated. A straight line is obtained for each separation factor and the lines for different separation factors are parallel.

Use of the graph will be illustrated by means of an example. Suppose that two substances have a separation factor (ratio of retention times) of 2.0, and that they are present in a 1:1 ratio. For this case $m_1 = m_2$ and the factor $\eta\,(m_1^2+m_2^2)/\,2m_1m_2$ is equal to η. One can determine from the graph the number of plates required to produce the desired purity. A fractional impurity of 1% (0.01) would require about 45 plates or the fractional impurity could be reduced to 10^{-5} by use of a column with 150 theoretical plates. If the substances are present in a 10:1 molar ratio, $\eta\,(m_1^2+m_2^2)/\,2\,m_1m_2 = 5.05$, and the number of plates required to obtain a fractional impurity of 10^{-5} is about 120. For a molar ratio of 100:1, about 90 plates are required for the same fractional impurity.

PERFORMANCE INDEX

In connection with the theory of gas chromatography in open capillary tubes, Golay has proposed the use of the Performance Index, which is calculated as follows (577):

$$P.I. = \frac{(\Delta \underline{t})^4\ \underline{t_a}\ \Delta \underline{p}}{\underline{t}^3\ (\underline{t}\ -\ 15\,\underline{t_a}/16)}$$

$\Delta \underline{t}$ is the peak width at half height, $\underline{t}$ is the retention time of a sample component, $\underline{t_a}$ is the retention time of air, and $\Delta \underline{p}$ is the pressure drop across the column.

Originally the Performance Index was introduced as a measure of "the intrinsic goodness of capillary columns operated at optimum flow rate." According to Golay the theoretical lower limit of the value of the Performance

Index is 0.1 poise. The smallest value obtained for actual capillary columns is 2.3 (577). For packed columns, the smallest value reported is 5.55 (640).

Chapter 3

MECHANISM OF SEPARATION

H. S. Knight

Shell Devolopment Company

AT THIS POINT it would be well to recall that there are two basic kinds of gas chromatography. One, called gas-solid chromatography (GSC), achieves a separation as a result of the varying adsorbability of the components of a mixture on some adsorbent. The other, called gas-liquid chromatography (GLC), is based on varying absorbability of the sample components in a liquid solvent impregnated on a support.

RELATIVE VOLATILITY

The separation in gas chromatography (GSC or GLC) takes place because the molecules of one component spend more time in the carrier gas than those of another, hence the former material is swept through the column faster. It is apparent then that separation is a matter of relative volatility (292). One factor that obviously affects the volatility is the vapor pressure, P^o. Other factors include adsorption and solute-solvent effects, and in some cases molecular weight. In the equation below, the relative volatility, α, is expressed in the usual manner as for distillation, but the activity coefficients are replaced by the non-committal $\underline{a}$'s, where $\underline{a}$ includes any factor affecting the volatility, and hence the separation, except vapor pressure.

$$\alpha_{21} = \frac{\underline{a}_2 P^o_2}{\underline{a}_1 P^o_1} = \frac{\text{Retention Time 1}}{\text{Retention Time 2}}$$

This equation will be used to interpret GSC and GLC separations as well as asymmetrical peaks. If the vapor pressures are known only the retention times need be obtained for calculation of $\underline{a}$ values. If $\underline{a}$ values for various columns are available, one giving a desired relative volatility can be selected. The retention times in the above equation must be corrected for the void space in the column, which is done automatically if they are measured from a peak representing an unabsorbed, unadsorbed material, such as air in GLC.

Application to Adsorption. In the adsorption or GSC case, $\underline{a}$ represents adsorbability primarily. On polar adsorbents there is a general agreement between adsorbability and the polarity of the molecule, where polarity may be measured by dipole moments or dielectric constants, or by solubility in polar solvents such as water. Amines, water and alcohols are most strongly adsorbed, followed by carbonyls, acids, esters, ethers, aromatics, olefins and saturates. The higher the molecular weight the lower the polarity and adsorbability. Among the hydrocarbons, degree of unsaturation can be correlated with adsorbability. Thus dienes are more strongly held than monoolefins, and highly unsaturated compounds like cyclopentadiene are more strongly held than benzene. The ring or chain structure also plays a role. In liquid phase work solute-solvent interactions can reverse the sequence, for example methyl alcohol is adsorbed from dilute solution in n-heptane (95). This causes the well known S-shaped adsorption isotherms. In GSC such interactions are negligible. In GSC the paraffin is always preferentially removed from a blend with a cyclane of the same carbon number, and methyl alcohol is more strongly adsorbed than n-heptane on polar adsorbents.

Nonpolar adsorbents such as activated carbon are also used in GSC. On carbon the adsorption of hydrocarbons is strong, and increases rapidly with molecular weight, so that this adsorbent is seldom used for C_2's and never for C_3's as far as the author is aware. The affinity of carbon for hydrocarbons is shown by the fact that methane emerges after carbon monoxide from a carbon column.

In practice, GSC is used almost exclusively for fixed gases. However, the adsorption of higher boiling compounds should be understood because adsorption affects GLC

separations in ways that will be taken up later.

In gas analysis, the vapor pressure ratio in the relative volatility equation is neglected because the column is practically always operated above the critical temperature. It is probably easier to determine the remaining $\underline{a}_2/\underline{a}_1$ ratio by GSC than to apply data from other sources to column selection.

There is one predictable factor that influences GSC separations to some extent, namely the molecular weights of the components. Large molecules are likely to diffuse into and out of the pores of the adsorbent more slowly than light ones. This effect becomes more important as the pores become deeper, particularly if the mouth of the pore is restricted.

An outstanding, relatively new class of polar adsorbents having pores with restricted openings is the Molecular Sieve series made by Linde Air Products. In the gas analysis work of Davis and Schreiber, described later, the molecular weight sequence is usually adhered to. Methane emerges before carbon monoxide on this support.

The Molecular Sieves influence separation in one other very important way, by excluding molecules that are too large to enter. The most common sieve in GSC is the 5A grade, having pores about 5 angstroms in diameter. Such pores will admit normal paraffins but will not admit branched chain compounds. Since petroleum products contain large amounts of normals, the 5A sieves are of great importance in the petroleum industry. For example, the normals are of low octane number and their determination in gasoline is of interest. Brenner and Coates (544) removed the normal paraffins from a C_4-C_{11} stream, using one foot of 5A sieve and a long partition column. They determined the normals by difference. Whitham (659) worked with higher boiling fractions, as will be discussed later.

Application to Partition. The mechanism of separation in GLC will now be discussed. In this case $\underline{a}$ represents primarily the activity coefficient of the sample component in the solvent. It is customary, though not always justified, to assume that there is no adsorption. The relative volatility equation then becomes (as in distillation):

$$\alpha = \frac{\gamma_2 P^o_2}{\gamma_1 P^o_1}$$

In GLC vapor pressure is very important, since the samples commonly have a critical temperature above room temperature. The two parameters, γ and P, are responsible at the same time for the scope and the complexity of GLC. The γ is the Raoult's law deviation factor, and it expresses the tendency of the solute molecules to escape from the solution to a greater or lesser extent than would be expected from their concentration and the vapor pressure of the pure solute. The γ ratio is a measure of the selectivity of the column for compounds 1 and 2.

Chromatographic Columns versus Distillation Columns. The question might arise as to why with modern columns having very large numbers of plates (high efficiency) there should be much interest in selectivity. In the first place, GLC plates are not to be compared directly with distillation plates. In a distillation column there is a uniform gradation of the volatile material from a low concentration at the bottom to a high concentration at the top. Each plate contributes something to the separation. In GLC the sample components pass through the column in a band which never under ordinary conditions fills the entire column. Only a small part of the column is actually engaged in separating the sample at any one time. Then the highly efficient columns have drawbacks in terms of convenience and analytical time, and will probably be used only where needed. The variables affecting efficiency are discussed in Chapters 2 and 6.

Further, selectivity is of interest in trace analysis. In this case large samples are necessary, and if the trace material can be made to emerge early, it will not be on the tail of the large peak. Ideally, it will form a relatively high, narrow peak which can be easily distinguished and measured.

Finally, there will always be cases where two or more materials have the same retention time on a particular solvent. This will occur whenever $\underline{a}_2/\underline{a}_1 = P^o_1/P^o_2$.

GLC is an analytical scale extractive distillation in that both vapor pressure and solvent-solute interactions can

influence the result. Vapor pressure data for use in the relative volatility equation are available from Jordan's book (94) or from API tables for hydrocarbons and simple derivatives. Pierotti et al. (287) have worked out an empirical method for calculating activity coefficients which might be used for a preliminary selection of promising columns. Their method is good to about 5%, but since GLC will separate materials whose volatilities differ less than 5%, final column selection is often empirical. The above approach assumes that adsorption is negligible. All in all, it is more likely that GLC will be used to calculate relative volatilities than that these will be available for use in column selection.

GLC normally involves volatile solutes and nonvolatile solvents, whereas in normal distillation the components for which relative volatility data are most needed will have similar volatilities. However, Kwantes and Rijnders (606) have shown that γ values can be determined by GLC where the solvent is only one carbon number different from the solute. They achieved this by saturating the carrier with the solvent to reduce loss during the experiment. They experienced some difficulty with adsorption. Their best results were obtained with nonpolar solutes in polar solvents (see Chapter 7).

Solute-Solvent Interaction. It is of interest to consider the order of magnitude of the activity coefficient ratio change with solvent. Taking water and n-heptane as an extreme example, the retention time ratio of these compounds will vary by a factor of 1000 as the solvent is changed from a hydrocarbon to glycerol. It will be shown shortly that among the C_6 hydrocarbons the naphthenes and paraffins may be shifted relatively by a factor of 3, the saturates and olefins by a factor of 2, and the saturates and aromatics by some 15 times.

Before going briefly into the nature of the interactions causing high or low γ values, it should be pointed out that GLC literature data will seldom be given in terms of relative volatilities. It is considered that the most common reason for consulting the literature will be to obtain information from which one can reproduce a given reported separation. The quantity best meeting this need is the partition coefficient H (not to be confused with the H in HETP) or a

closely related quantity V_g, the specific retention volume. Detailed discussions of terms, units and methods of presenting data have been given by Ambrose, Keulemans and Purnell (529) and by Johnson and Stross (598). Many practical gas chromatographers will probably continue to think in terms of retention times or inches of chart.

Since activity coefficients will seldom be available with sufficient accuracy to permit selection of a specific solvent for a given difficult separation, it is important to know how to proceed if the column being tried is unsatisfactory from the standpoint of selectivity. In general, the approach is to vary the solvent's affinity for the solutes in a systematic way to improve the separation.

Keulemans, Kwantes and Zaal (136, 439) have discussed the problem more or less from this point of view. The forces affecting solubility include (1) forces between permanent dipoles, (2) forces between a permanent and an induced dipole, and (3) nonpolar forces. These concepts are readily used to explain the variation in separation of cyclohexane and benzene as the solvent increases in polarity.

On a paraffin (nonpolar) solvent, benzene emerges earlier than cyclohexane because the benzene molecules do not interact with each other as they do in pure benzene. Hence benzene in dilute solution in paraffin assumes a lower boiling point, in accord with its lower molecular weight, and benzene emerges ahead of cyclohexane. On a phthalate ester solvent benzene becomes polarized, its activity coefficient goes down, and it emerges after cyclohexane.

A common interaction is the hydrogen bond. With a polyglycol solvent the primary, secondary and tertiary amines form successively weaker hydrogen bonds (higher activity coefficients) whereas a paraffin solvent separates them by boiling point.

In the previous discussion selectivity has been presented in terms of activity coefficients. In the literature other ways of showing selectivity are common. The boiling point or vapor pressure or carbon number may be plotted against the log of the retention time, retention volume, or H value, for various homologous series. The result is a series of lines or gentle curves, which differ on the time axis according to selectivity. An interesting way to compare two solvents is to plot the log of the partition coeffi-

cient obtained on one against similar data for the other. A series of parallel lines is obtained (287) for the various homologous series. One point for a new series establishes the line for that series. However, on any of these plots the first few members may be out of line.

Instead of plotting retention time or partition coefficients, relative times are often used. Tenney (649) used n-pentane as a standard with an assigned time of unity, and calculated the retention times of other materials on this basis. Similarly, Knight (603) used 1-hexene or methyl alcohol as a standard having an assigned a value of unity. The use of a standard can simplify column comparisons within any one laboratory, although there are valid arguments against this practice if the data are to be published.

In this chapter we have emphasized selectivity, but of course there are occasions when nothing more is desired than a good boiling point separation. In practice something in between is often the best. Consider the slide rule, one portion of which can be moved relative to the rest. So it is with selective solvents - one molecular type spectrum can be moved relative to the others. If sufficient selectivity is available complete separation will result. The separation within each type will be more or less by boiling point. In many cases, however, the movement is small and one set of unresolved peaks is simply exchanged for another set. If the sample is not too complex it may be possible to control the selectivity so that peaks of one type appear among peaks of the others without actually conflicting. Examples of this and other approaches will be taken up in Chapter 8.

Chapter 4

MOBILE PHASE

S. A. Greene

Rocketdyne Research

IN CONSIDERING THE TYPES OF GASES which could serve as carriers, one must first determine the role of the mobile phase. The theory of gas-liquid chromatography developed by Martin and Synge (5) introduces hardly any new concepts differing from those of liquid chromatography. It has been suggested that gas chromatography differs from liquid chromatography only in that the mobile phase is compressible (44) and the carrier gas undergoes an acceleration through a packed column. The advantages of a gas as a mobile phase are the following (243): (a) high rates of diffusion in the gas phase allow equilibrium with the liquid to be rapidly attained, (b) the compressibility of the gas allows the convenience of long thin columns even at rapid rates of flow, (c) it is easier to detect vapors in permanent gases than solutes in solvents, particularly in the case of such unreactive substances as saturated hydrocarbons, (d) high column efficiencies are attainable even at rapid rates of flow, so that precise separations can be carried out more rapidly than by any other technique.

THEORETICAL CONSIDERATIONS

The mechanism of separation of gases by gas chromatography and the function of the carrier are quite amenable to a mathematical analysis using a simple, but realistic model. The problem is to describe the rate of movement

of a concentration zone through a partition or adsorption column in terms of operating variables. Variables of interest are column geometry and material, column temperature, and the type of carrier gas and its flow rate. These should explicitly define the retention time. The technique will be to view the movement of a concentration zone as a rate process. Since every rate process has an activation energy, the model will predict an activation energy. It will also be shown that this "mechanical" or "kinetic" approach yields an activation energy which permits insight into the mechanism of chromatography.

Kinetic Approach. For gas-solid chromatography we assume an array of adsorption sites within the column with a moving concentration zone consisting of adsorbed gas always in the same dynamic equilibrium with gas in the vapor phase. Gas molecules cannot move when adsorbed, but only when in the vapor phase, and do not lag behind the carrier gas which is not adsorbed. When a zone is in dynamic equilibrium between a gas and solid phase, it can easily be shown that the fraction of time spent by each zone molecule in the gas phase is given by the expression:

$$\frac{\underline{n}_g}{\underline{n}_g + \underline{n}_a} \qquad (4\text{-}1)$$

where $\underline{n}_g$ = moles of zone in gas phase, and
$\underline{n}_a$ = moles of zone adsorbed

Thus,

$$\underline{u} = \underline{u}_g \frac{\underline{n}_g}{\underline{n}_g + \underline{n}_a} \qquad (4\text{-}2)$$

where $\underline{u}$ = linear velocity of concentration zone, and
$\underline{u}_g$ = linear velocity of carrier gas

which is seen to have the correct boundary conditions. The model states simply that at any instant a zone molecule is either on the surface or in the gas phase. It may move with the carrier only when in the latter phase and its halting journey through the column may be described by an average linear velocity.

The equilibrium constant for adsorption is:

$$H_a = \frac{\underline{n}_a}{\underline{n}_g} \tag{4-3}$$

and substituting into equation 4-2, we have:

$$\underline{u} = \underline{u}_g \frac{1}{H_a + 1} \tag{4-4}$$

since $\underline{u} = \frac{\underline{l}}{\underline{t}_R}$ and $\underline{u}_g = \frac{F_c}{\underline{a}}$

we substitute these values in equation 4-4, and obtain:

$$\underline{t}_R = \frac{\underline{l}\underline{a}}{F_c} (1 + H_a) \tag{4-5}$$

where $\underline{l}$ = packed length of adsorption column
$\underline{t}_R$ = retention time of zone
$\underline{a}$ = interstitial area of column
F_c = flow rate of carrier gas

Since the interstitial volume of the column, V_G^o, is equal to $\underline{l}\underline{a}$, equation 4-5 becomes:

$$\underline{t}_R = \frac{V_G^o}{F_c} (1 + H_a) \tag{4-6}$$

For parameters usually encountered in equation 4-6, H_a is much larger than unity and

$$\underline{t}_R = \frac{\underline{l}\underline{a} H_a}{F_c} \tag{4-7}$$

Utilizing the temperature dependence of H_a

$$B \exp\left(- \frac{Q_a}{RT}\right) \tag{4-8}$$

and substituting in equation 4-7, we have

$$\underline{t}_R = \frac{laB}{F_c} \exp\left(-\frac{Q_a}{RT}\right) \qquad (4\text{-}9)$$

where B = a constant
Q_a = heat of adsorption of zone on adsorbent

An analogous treatment of gas-liquid chromatography results in an expression similar to equation 4-6:

$$\underline{t}_R = \frac{V_G^o}{F_c}\left(1 + \frac{HV_L}{V_G^o}\right) \qquad (4\text{-}10)$$

or

$$V_R^o = V_G^o + HV_L \qquad (4\text{-}11)$$

where $V_R^o = F_c \underline{t}_R$ = limiting retention volume

$V_G^o = \underline{la}$ = volume of gas phase in column

V_L = volume of liquid phase in column

H = partition coefficient, ratio of concentration of solute in liquid and gas phase

From equation 4-8, we derive:

$$\underline{t}_R = \frac{la}{F_c}\left[1 + C \exp\left(-\frac{Q_s}{RT}\right)\right] \qquad (4\text{-}12)$$

where Q_s is the heat of solution of the eluted gas in the liquid phase. If solutions are ideal, Q_s may be replaced by Q_v, where the latter is the heat of vaporization of the gas.

From equations 4-9 and 4-12 it is seen that retention time is inversely proportional to carrier gas flow rate, directly proportional to column length and exponentially proportional to temperature. The variation of retention time in this fashion has been shown by various authors (323, 582) for both gas-solid chromatography and gas-liquid chromatography.

From equation 4-10 it can be deduced that the re-

tention time is made up of two terms; the amount of time a gas molecule spends in the gas phase, V_G^o/F_c , and the amount of time in the liquid phase, HV_L/F_c. Note that both equations 4-6 and 4-10 are general equations, saying nothing of the carrier or eluted gas, and that only the partition or adsorption coefficient is responsible for separation of gases. Furthermore, in eluting a series of gases from a single column, the amount of time spent in the gas phase is identical for all gases, but the amount of time in the liquid or solid phases is variable.

Determination of Heat of Adsorption or Solution.

From equations 4-9 and 4-12 it can be seen that a plot of ln retention time corrected for the amount of time in the gas phase versus $1/T$ should yield the heat of adsorption of an eluted gas on the column packing for adsorption columns and the heat of solution (vaporization if ideal solutions are formed) in the liquid of partition columns. The latter plot must, of course, be corrected for the coefficient of expansion of the liquid phase. The heats have been derived and shown to agree quite well with those obtained by independent methods. Heats derived for n-butane from the slope of the straight line plot of $\ln \underline{t}_R$ versus $1/T$ are shown in Table 4-1 (582).

TABLE 4-1. HEATS OF n-BUTANE DERIVED FROM TEMPERATURE COEFFICIENTS OF RETENTION TIMES

Column Material	Heat (Cal/mole)
Activated alumina	8700
Di-n-ocytl phthalate (on Celite)	5360
Triisobutylene (on Celite)	5530

The derived heat of adsorption would seem to be reasonable for coverages at or less than one monolayer. The heat of adsorption of n-butane or alumina at 0°C has been determined from BET parameters as 8200 cal/mole (323). The heat of solution derived from the partition columns is in fair agreement with the heat of vaporization of n-butane. The heat of vaporization at the average temperature of the experiment was 5100 cal/mole (421).

Since the activation energy of the chromatographic process is associated with zone molecules entering and leaving the liquid, apparently diffusion can play only a second order role.

Partition or activity coefficients have been determined utilizing equation 4-9 (110, 292, 636) and agree well with partition coefficients derived directly from equilibrium methods. Note also from equations 4-5 and 4-8 that the retention volume is independent of flow rate.

Since the activation energy of the chromatographic process is apparently associated with zone molecules entering or leaving the surface for both gas-solid and gas-liquid chromatography, diffusion in the liquid phase is expected to play only a second order role. Diffusion controlled processes are proportional to the square root of the absolute temperature and the retention time would have been essentially insensitive to temperature over the relatively small temperature range utilized in the experiments illustrated in Table 4-1.

EFFECT OF CARRIER GAS ON RETENTION TIME

From equations 4-9 and 4-12, it can be seen that carrier gases might play a relatively minor role in influencing separations. Their only contribution could be to affect either the heat of solution or adsorption of the concentration zone and thus the retention time. The effect may be appreciable since the dependence is exponential.

Effect with Partition Columns. For gas-liquid chromatography the more cryogenic carrier gases such as helium, hydrogen, argon, or nitrogen will be negligibly soluble in the liquid phase and will thus not effect the heat of solution. Use of such gases as acetylene, propane, or

butane are expected to exhibit solubility in organic phases, but such experiments would be academic, since it is simpler to modify heats of solution by addition of other liquids to the partitioning phase.

Effect with Adsorption Columns. For gas-solid chromatography carrier gases can theoretically have a pronounced effect on retention time. Charcoal, a common adsorbent, can adsorb at room temperature appreciable quantities of typically used carrier gases such as nitrogen, argon, and carbon dioxide. We postulate a fixed number of adsorption sites, admit the possibility of carrier gases competing for the sites, and question the effect on retention time. Qualitatively, if carrier gas is adsorbed, one would expect the retention time to be reduced. A simple argument would suggest that if adsorption sites can also be occupied by adsorbed carrier gas then the total amount of time a zone molecule spends at a given site can only be reduced. Thus, the effective length of the column is reduced as is the retention time as predicted by equation 4-5. If a series of carrier gases which were adsorbed in increasing amounts, were used to elute a gas, then the retention time of the eluted gas would be reduced increasingly. The phenomenon has been verified (405) and is illustrated in Table 4-2. Heats of adsorption obtained with carriers which are adsorbed are shown in Table 4-3. It is seen that the derived heat of adsorption is decreased, the decrease caused being greater for those carriers which would be expected to be adsorbed to the greatest extent. Equation 4-9 predicts the decrease in retention time as the derived heat of adsorption is lowered. In spite of these experiments, the factors causing decreased retention time are not completely understood. It is possible for the retention time to be reduced while the heat of adsorption is unaffected as in the case of a homogeneous surface in the absence of adsorbate interactions.

From Table 4-4 it can be seen that in the case of ethylene and acetylene, the derived heats of adsorption are comparable to heats of vaporization. Thus, adsorbed carrier gases have completely destroyed the adsorption properties of the adsorbent and what corresponds to a gas-liquid partition column results. Adsorbed carrier gas is pictured to be deposited on the adsorbent surface as a liquid-like film.

TABLE 4-2. EFFECT OF CARRIER GAS ON RETENTION TIMES OF METHANE

Carrier Gas	Retention Time, min*
Helium	34
Argon	22
Air	15
Nitrogen	16
Acetylene	5

*Retention times of methane on a 10-ft charcoal column at 25°C, flow rate of carrier gases is 70 cc/min.

Further exploitation of this technique is expected to increase the power of gas chromatography. Carrier gases such as hydrogen chloride, hydrogen sulfide, or hydrogen cyanide could be utilized to deposit liquid-like films on adsorbents for specific separations.

Since the adsorption of carrier gas reduces the retention time of eluted gases, the time between eluted peaks will be less and separations in general, less clean. Janak (68) used carbon dioxide as a carrier gas and adsorbed the effluent in potassium hydroxide, volumetrically recording the eluted gases. If one reviews his separations on both silica gel and alumina and compares them with those of Greene and Pust (403) obtained by using helium, one is immediately impressed by the effect of carrier gas adsorption on separation efficiency. This is especially evident with alumina, since the adsorbent irreversibly adsorbs carbon dioxide.

SELECTION OF CARRIER GAS

Detector Considerations. Gas chromatographic instruments usually employ thermal conductivity cell detectors, either of the hot wire or thermistor type. Thus, the larger the difference between the thermal conductivity of carrier and eluted gas, the larger is the signal. The kinetic

theory of gases states that the thermal conductivity of a gas is inversely proportional to the square root of the molecular weight. The two lightest gases, hydrogen and helium, are excellent candidates for carrier gases since they are readily available in pressurized cylinders, inexpensive, and farthest removed in thermal conductivity from other gases. Table 4-5 lists the thermal conductivities of various gases of interest.

TABLE 4-3. EFFECT OF CARRIER GAS ON DERIVED HEATS (Kcal/mole)

A. ALUMINA
Carrier Gas

	He	C_2H_2	C_2H_4
C_3H_8	7150	3320	4000
C_4H_{10}	8700	3400	——

B. SILICA GEL
Carrier Gas

	He	C_2H_2
CO_2	6290	2400
C_3H_8	8060	3230

C. CHARCOAL
Carrier Gas

	He	N_2	Ar	CH_4
CH_4	4840	4100	3500	——
CO	3350	3000	2500	2000

TABLE 4-4. COMPARISON OF DERIVED HEATS OF ADSORPTION AND HEATS OF VAPORIZATION

GAS	CARRIER	HEAT (cal/mole)	ΔH_v* (cal/mole)
C_3H_8	C_2H_2	3230	3640
CO_2	C_2H_2	2400	2090
C_3H_8	C_2H_2	3320	3640
C_3H_8	C_2H_4	4000	3640

*Ref. 421.

Hydrogen, helium, and nitrogen offer adequate sensitivity for analysis of all organic vapors. For analysis of inorganic gases, oxygen, argon, and neon in addition to those already mentioned.

Sample column material and detector elements should be inert to the carrier gas. Glycol-silver nitrate columns used to separate ethylene and ethane (110) are rapidly reduced by hydrogen at room temperature. Carrier gases which are expected to have a deleterious effect on filaments should not be used, or if necessary, the operating temperature of the filaments reduced.

Hydrogen gas would be expected to hydrogenate carbon dioxide, oxygen and unsaturated hydrocarbons at the surface of hot wire filaments. An explosion hazard is possible with the use of hydrogen, and the column effluent should be properly vented.

Cost of Gas. The cost of carrier gases is usually low and has a minor consideration. An expensive carrier gas, such as neon, is used for some special separations. Operating costs at 20 ml/min. flow are $12 per hour for carrier gas alone.

Effect on Sensitivity. There are instances where the similarity between thermal conductivity of carrier and an eluted gas reduces the sensitivity to such an extent that the analysis is not reliable. Complications arise when attempting to analyze hydrogen using the more standard carrier gas helium. The thermal conductivities are so similar that little sensitivity results and the analysis cannot be made with precision. Table 4-6 lists the response of various gases to candidate carriers. Those marked with an asterisk show adequate sensitivity for quantitative analysis.

TABLE 4-5. THERMAL CONDUCTIVITIES OF VARIOUS GASES AT 0 °C

Gas	Thermal conductivity* Cal./cm. sec. °C x 10^5
Hydrogen	39.60
Helium	33.60
Nitrogen	5.68
Oxygen	5.70
Carbon Dioxide	3.393
Carbon Monoxide	5.425
Isopentane	2.912
Argon	3.88
Neon	10.4
Nitric Oxide	5.55

*Lange, N.A., HANDBOOK OF CHEMISTRY, (1949)

TABLE 4-6. SENSITIVITY OF GASES TO VARIOUS CARRIERS.

	H_2	He	Ar	N_2	Ne
H_2			*	*	**
He			*	*	**
CO	*	*	*		*
CO_2	*	*	a	**	*
O_2	*	*	*		*
NO	*	*	*		*
N_2	*	*	*		*
Ar	*	*		*	*
HC	*	*	*	*	*

HC - Hydrocarbons
* - Adequate sensitivity for quantitative analysis
** - Signal will be negative as compared to other gases
a - Sensitivity depends markedly on filament current

Effect on Separation. Probably the most troublesome gas mixtures to analyze are those from flames, which include hydrogen, oxides of carbon, nitrogen, and some hydrocarbons. In order to avoid duplicate runs with different carrier gases, neon might be utilized. Although the gas is expensive ($1.00/liter), the advantages have been found to outweigh the price. There are some special separations for which only neon is adequate. For example, it was desired to separate small concentrations H_2, HD, and D_2 in helium (700). Obviously helium could not be utilized as the carrier since there would not have been adequate sensitivity. For any separation at all, the temperature of the separation would need to be reduced considerably, using a charcoal

column immersed in liquid oxygen. Carrier gases such as nitrogen and argon were utilized, but no separations were obtained. It was theorized that the carriers were adsorbed to the extent that a liquid-like film formed on the charcoal surface, and in effect a partition column resulted. The same separations were attempted with neon carrier gas with partially successful results. Helium, hydrogen (both ortho and para) were well separated, but HD could not be completely separated from D_2. The separations were attempted at liquid nitrogen temperatures, and with silica gel and alumina, with essentially the same results.

The separation of hydrogen and helium can be accomplished on charcoal at room temperature on twenty foot charcoal columns utilizing either argon or nitrogen as the carrier gas. The wave form of hydrogen is interesting in that it has a leading front and sharp back. With argon or nitrogen one must utilize long columns, or reduce the temperature of shorter ones to $0^{o}C$ in order to separate cleanly hydrogen and nitrogen. Use of neon produces a completely symmetrical hydrogen peak form and hydrogen and helium are separated at room temperature in short columns.

The separation of argon and oxygen has not been reported on any of the more common adsorbents. Greene (700) has utilized oxygen carrier to blank out the oxygen contained in argon-oxygen mixtures and the oxygen was determined by difference.

It is interesting that elution of small samples of hydrogen with helium results in a signal where polarity indicates that hydrogen has a thermal conductivity less than that of helium. As the sample size is continuously increased, a minimum appears in the wave form which ultimately becomes negative with respect to the baseline (616). The total signal is then composed of two positive peaks and a negative one. The same effect has been observed utilizing oxygen as the carrier with large samples of nitrogen (700) and is apparently associated with similarity in the thermal conductivity of carrier and eluted gas.

CARRIER GAS FLOW RATE

Control of carrier gas flow rate is easily accomplished by control of a pressure drop almost anywhere in

the flow circuit. Commercially available pressure regulators such as those manufactured by the Conoflow Corporation or the Fischer and Porter Company are adequate for setting a constant pressure to the head of the column.

Control Requirements. Various investigators report the effects of carrier gas flow rate on detector response. Percival (475) says that column flow rate must be controlled to 0.2% in order to keep the error in analyses below 0.5%. Similar results are reported by Dimbat and co-workers (198), who claimed that flow rate must be controlled to 1% in order to reduce the analytical error below 1%. Both detectors are typical of those used in gas chromatography and the results are probably representative. The simplest and least expensive instrument from which one can determine pressure changes (and hence flow rates) of 0.5-1% is the differential manometer, preferably reading a differential at least 200 mm. When carrier gas flow rates are measured by a pressure drop at the column exit using a differential manometer, the elution of a peak will cause a pressure surge in the manometer due to the change in viscosity of gas flowing through the restricting orifice. The phenomenon could possibly be utilized as a method of detection.

Effect of Flow Rate on Peak Height, Area, and Shape. Retention time is used to identify components emerging from columns. Therefore, it is essential that flow rate be known or constant. For quantitative analysis the flow rate should be precisely controlled because of the effect on detector signals. If carrier gas is permitted to pass over the filaments at varying rates, then the amount of heat removed by the carrier from the filament will be variable, as will be filament temperature, response and sensitivity. There are, however, cell geometries which minimize the effects of fluctuations in flow, but the effect is a spurious one and not amenable to mathematical treatment.

Flow rate has a definite intrinsic effect on peak area which may be predicted from simple mechanical considerations. Consider a recorder which amplifies the detector cell output and has a constant chart speed. The filaments are in the directed path of the carrier flow. The sensitivity is linear and independent of flow, and the response

is measured at a given flow for a given amount of eluted gas. We define the response, or peak area, as

$$r = g\ m\ s\ C_1\ C_2/C_3$$

where r = response = peak area, mv x min
g = proportionality constant
s = detector sensitivity, mv/weight of solute, a constant
m = weight of solute introduced to column
C_1 = chart speed, cm/min
C_2 = detector amplification factor
C_3 = carrier gas flow rate, ml/min

The detector sensitivity is assumed to be a constant and depends only on the thermal conductivity of carrier and solute, and the properties of the filaments. We repeat the experiment with the same amount of solute but at twice the carrier gas flow rate and note the effects on peak height, peak width at the base line, and peak area. The peak height was found to remain constant while the area was halved utilizing gas-liquid partition techniques (198), suggesting the base line to be halved when a triangular approximation to the peak form is assumed. Percival (475) found the product of the peak area and flow rate to be relatively insensitive to flow utilizing gas adsorption techniques.

One might expect this inverse relationship between carrier flow (linear velocity) and peak area. When the carrier gas flow rate is doubled, its linear velocity is approximately doubled and the detector responds to the identical varying concentrations of solute on a time scale that is condensed by a factor of one-half. The peak height observed in the second experiment would not be expected to change, since carrier gas flow has theoretically no effect on the partition coefficient or the partial pressure of an eluted gas.

Effect of Carrier Gas Flow Rate on Separation.

From equation 4-5 it is seen that the retention time is inversely proportional to the carrier gas flow rate. The components of a gas mixture travel through a given column at a given carrier gas flow at velocities which are a function only of their partition coefficients. It is obvious that a

longer column at constant carrier gas velocity, or a slower carrier gas velocity at constant column length, will result in a better separation of the components. It is the relative linear velocities of zones in columns which ultimately permits their separation. Thus, if the ratio of retention volumes of two gases are determined at a given flow rate, theoretically the ratio will be the same at any other flow rate, greater or smaller. However, the separation as determined qualitatively by the distance between zone peaks, will be different. The idea is illustrated in Table 4-7 where theory indicates that separation improves with decreasing carrier flow rate on a given column.

TABLE 4-7. THEORETICAL VARIATION OF RETENTION TIME AND SEPARATION OF TWO GASES WITH CARRIER FLOW RATE

Flow Rate	1000	200	100	50	10
$\underline{t}_R$(Gas A)	0.2	1	2	4	20
$\underline{t}_R$(Gas B)	0.5	2.5	5	10	50
Separation*	0.3	1.5	3	6	30

*$\underline{t}_R$ gas B - $\underline{t}_R$ gas A

In reality, one cannot continually decrease the carrier gas flow rate in order to improve the separation of two gases. Aside from lengthening analysis time, there exists a region of diminishing return in decreasing flow rate. The retention time is inversely proportional to flow rate, and although the peak positions are pushed farther apart by decreasing flow, diffusional peak spreading may become so severe that separation is in reality not improved in return.

The resolving power limit is attained when conditions are such that increased retention time broadens two adjacent peaks at the same rate as their peaks are separated. When this happens a different or modified partition

liquid must be used in order to improve separation.

Separation Efficiency and Carrier Gas Flow Rate. The concept of the number of theoretical plates in a liquid chromatographic column was developed by Martin and Synge (5) and may be directly applied to gas chromatography. Qualitatively the concept is simply a measure of the amount of zone spreading during transit through a chromatographic column. We must be cautious in defining efficiency (plates) and resolution. The former is theoretically capable of exact mathematical computation, and is an indication of zone spreading, not separation, as in an ordinary distillation column. The latter term refers to the degree of separation of gases. We can have chromatographic columns with an enormous number of plates, while the resolution of some gases is quite poor. As described in Chapter 2, the number of theoretical plates in a gas chromatographic column is determined from the expression: $\underline{n} = 16\,(\underline{t}_R / \Delta\underline{t})$. The expression is derived from chromatographic theories which predict the shape of an eluted zone and picture the separation process to be analogous with that in a distillation column. Mass transfer rates are infinite, diffusion is neglected, and band broadening is proportional to the square root of the number of theoretical plates. The mechanisms of band broadening are not contained within the theories. Both $\underline{t}_R$ and $\Delta\underline{t}$ are inversely proportional to flow rate, and the number of theoretical plates should be independent of flow rate.

The more elaborate theory of gas chromatography developed by van Deemter et al.(316) takes into account mass transfer and diffusion, and results in an expression which shows the dependence of HETP on carrier gas flow rate. The familiar van Deemter equation indicates the HETP to consist of three contributions, and may be written in the following simplified form: $\text{HETP} = A + B/\underline{u} + C\underline{u}$.

The phenomenon of band broadening, that is, HETP, will be minimum at a certain carrier gas flow rate and at that flow rate, the separation efficiency will be greatest. The effect of carrier gas flow rate on the separation of o- and p- xylene (276) is illustrated in Fig. 4-1.

Hydrogen and helium stand apart in their low molecular weights and hence high diffusivities. Gases diffuse

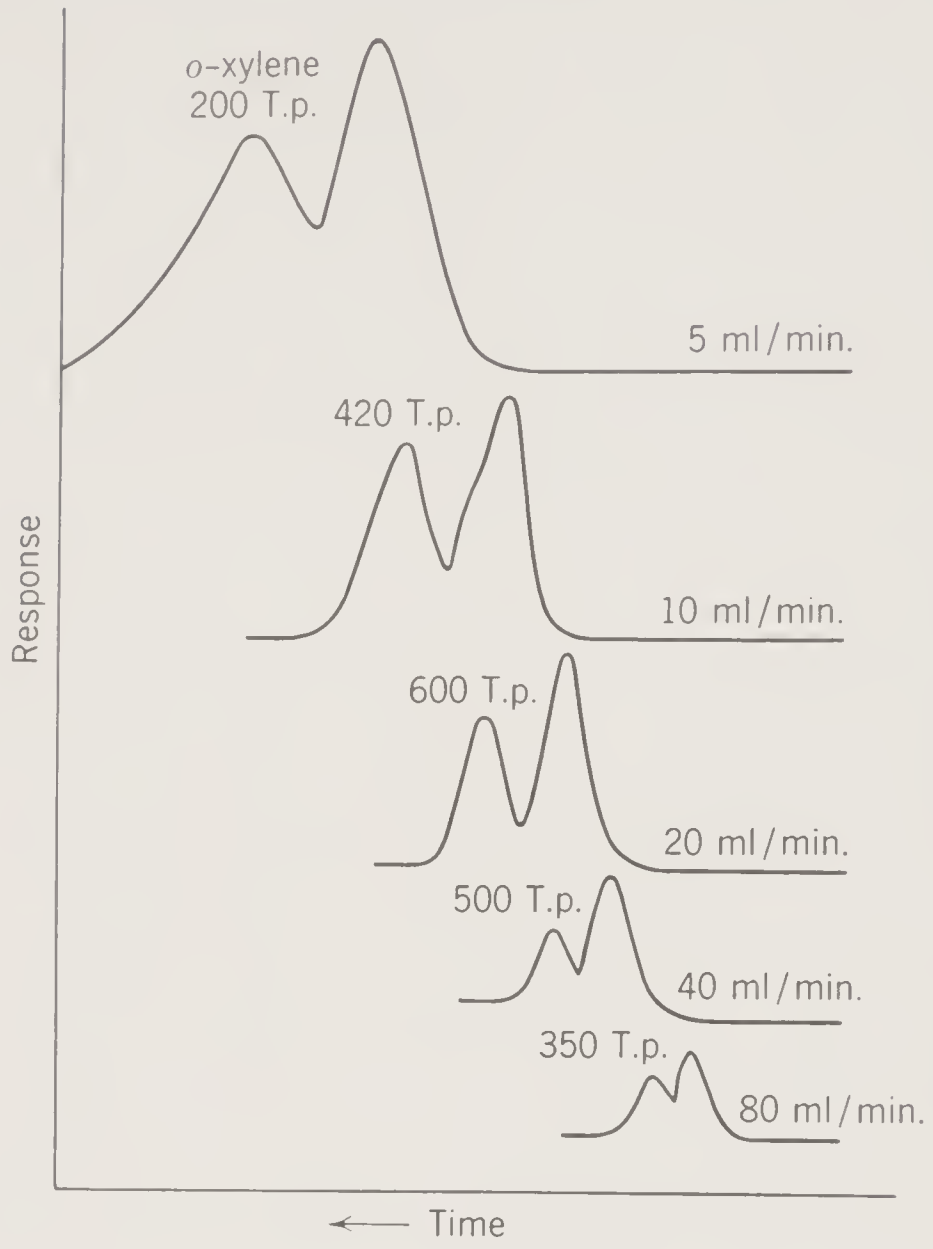

Fig. 4-1. Separation of o- and p-xylene. After Mellor (276).

3-4 times as rapidly through hydrogen than through nitrogen. Peak broadening caused by diffusion in hydrogen would be expected to be more pronounced than in nitrogen and the latter would be the preferred carrier gas provided sensitivity was adequate. It has been found (171) that clean separations of propane and propylene could be obtained with nitrogen carrier while hydrogen produced severe overlapping. The separations are illustrated in Fig. 4-2.

Retention Time and Pressure-Flow Relations. Since there is a pressure drop across gas chromatographic column, the carrier gas as well as the eluted zone will undergo an acceleration as they pass through the column.

In order to determine heats of solution and partition coefficients, and to standardize retention volumes determined experimentally, it is necessary to deduce a reten-

tion volume that is independent of the pressure change along the column. The retention volume obtained by multiplication of retention time and carrier flow as measured at the column exit is a true constant only when there is a negligible pressure drop across the column. The concept is illustrated in Table 4-8 where the term, $F_c \underline{t}_R$, the experimentally determined retention volume, is shown as a function of pressure ratio or its adjunct, flow rate across the column. It is assumed that the pressure at the column exit will be one

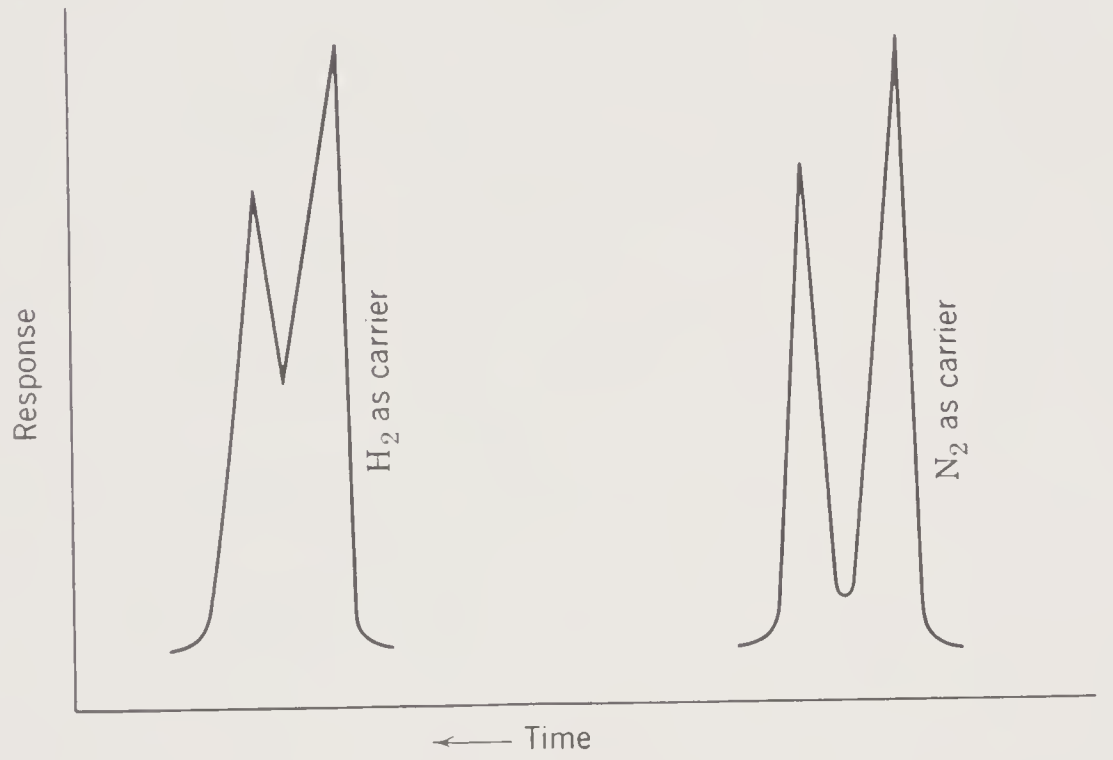

Fig. 4-2. Separation of propane and propylene with 30% triisobutylene on Celite. After Bosanquet and Morgan (171).

TABLE 4-8. EFFECT OF PRESSURE RATIO ON OBSERVED RETENTION VOLUME

p_i/p_o	$F_c \underline{t}_R$
1.00	1.00
1.02	1.01
1.05	1.03
1.10	1.05
1.50	1.27
2.0	1.56
3.0	2.16
4.0	4.2

atmosphere and 25°C. The complication arises simply because gases are compressible and will be resolved by computing the limiting retention volume V_R^o, which is the retention volume which would have been observed at zero pressure drop across the column.

The correction factor for pressure drop across the column has been derived by James and Martin (44, 47). The average pressure in the column is given by:

$$\bar{p} = \frac{2}{3} p_o \frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1}$$

and the limiting, or corrected, retention volume is given by

$$V_R^o = V_R \frac{3}{2} \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}$$

and

$$V_R^o / V_R = p_o/\bar{p} .$$

Chapter 5

STATIONARY PHASE

H. S. Knight

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THE CHARACTERISTICS OF ADSORBENTS for use in GSC are very similar to those for liquid phase chromatography, and include adequate surface area, reasonable particle size and chemical inertness. Many established liquid phase adsorbents have simply been taken over for GSC.

ADSORBENTS FOR GAS-SOLID CHROMATOGRAPHY

Activated Carbon. Madison (616) used activated carbon to separate the fixed gases, hydrogen, oxygen, nitrogen, carbon monoxide and methane (Fig. 5-1). His col-

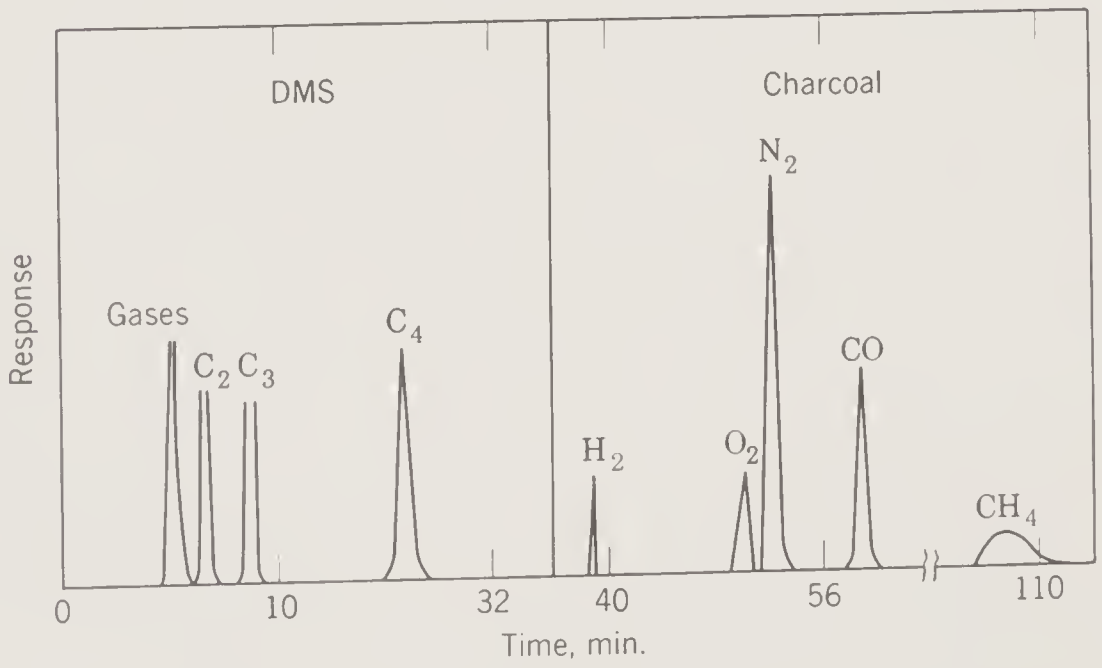

Fig. 5-1. Two-stage separation of gases and light hydrocarbons. Courtesy of Analytical Chemistry (616).

umn was 25 ft. long and was operated at 20°C. His work is of special interest because he used a two-column technique with only one thermal conductivity detector and recorder. A liquid partition column separated the above gases from ethane and propane, and the gases were trapped in a short column of activated carbon maintained at liquid nitrogen temperature. The trap was disconnected while the ethane and propane emerged. Then the trap, the long carbon column and the detector were connected, and the carrier passed through the assembly while the trap was warmed. The gases were released to be separated by the carbon column.

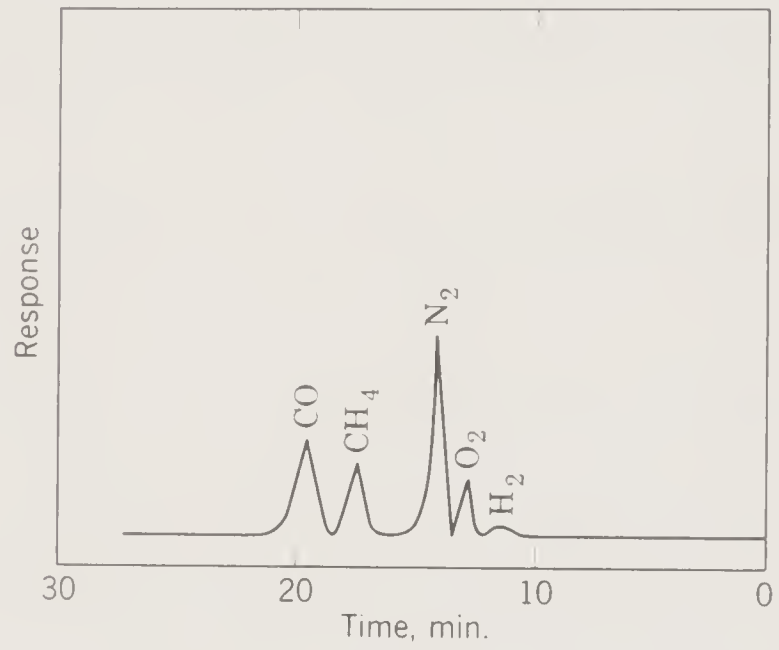

Fig. 5-2. Separation of gases on Molecular Sieve 5A. Courtesy of American Chemical Society (362).

Madison observed positive peaks for hydrogen in small amounts, but negative peaks with positive front and back sections for large amounts of hydrogen. The reasons for this were discussed in Chapter 4.

Molecular Sieve. Davis and Schreiber (362) developed a more elaborate two-column separation using two detectors and recorders. Their GLC column will be described later. They used Molecular Sieve 5A for the gas analysis portion. Their column was 15 ft. long and was held at 100°C (Fig. 5-2). Note that the gases emerged in 20 min as opposed to 60 min on activated carbon, and that methane was ahead of carbon monoxide. Carbon dioxide was determined by these workers on their partition column.

Greene (583) also used Molecular Sieve 5A for gas analysis. He deliberately violated the rule about chemical inertness of the support to determine nitrogen dioxide. This gas does not emerge from an ordinary GSC column and tails badly in GLC. Greene added two ml of water to the inlet end of the Molecular Sieve column to bring about these reactions:

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

The nitric oxide peak was then used as a measure of the nitrogen dioxide originally present. After correcting for the equilibrium reaction:

$$2\ NO_2 \rightleftharpoons N_2O_4$$

the results were about as expected.

Silica Gel and Alumina. Silica gel was employed by Smith et al. (642) as the adsorbent in a chemically-aided separation of carbon monoxide or nitric oxide from nitrogen. Ordinarily silica gel does not separate these gases. A short section in the middle of the column was packed with iodine pentoxide followed by silver metal to react with any iodine released. If carbon monoxide was present it was converted to carbon dioxide in the middle of the column. The entire column separated the carbon dioxide in the original sample, and the second half separated the carbon dioxide representing the original carbon monoxide to half as great an extent.

In the case of nitrous oxide the oxidation product was nitrogen dioxide which failed to emerge from the dry column. The amount of nitrous oxide was determined by difference, by comparing a similar analysis without the oxidant in the column.

Patton et al. (151) separated low boiling hydrocarbons through C_5 by GSC and employed calibration factors to convert peak heights to concentrations. Fig. 5-3 shows that the later peaks tended to be distorted more and more. Such distortions usually restrict GSC to light gases.

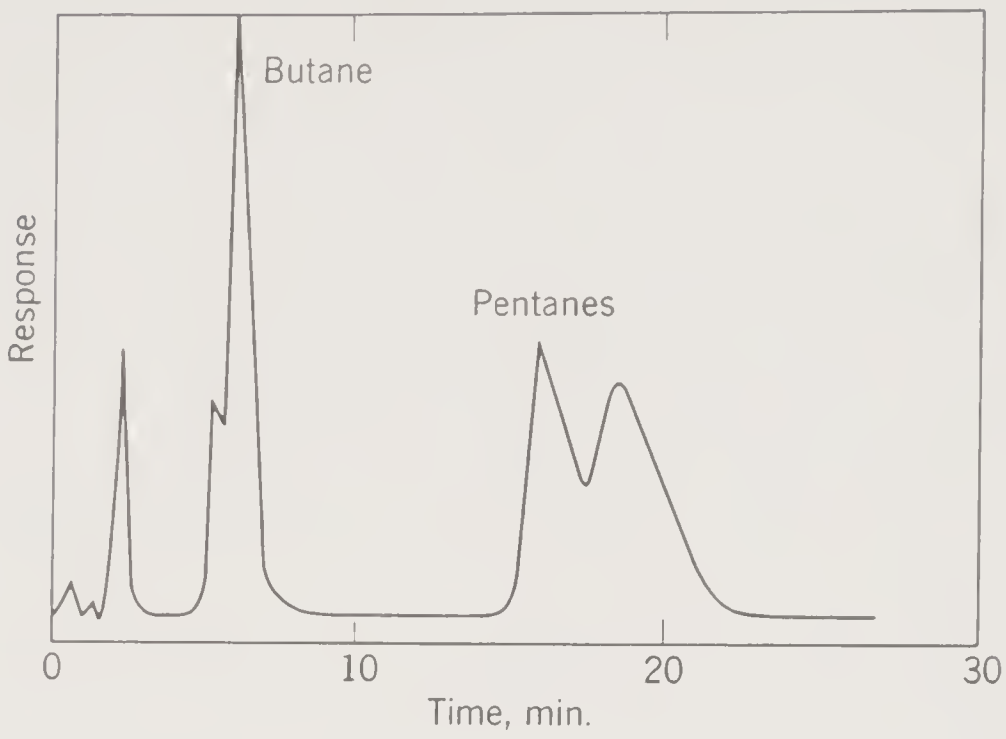

Fig. 5-3. GSC separation of hydrocarbons. Courtesy of Analytical Chemistry (151).

Greene and Pust (403) were able to work with fixed gases and up to C_4 by operating the 20 ft. silica or alumina column at a continuously increasing temperature. The fixed gases began emerging at 5°C and the butanes were completed at 150°C an hour later. The volatility of the material represented by the tail was raised by the higher temperature, reducing the tail. As a matter of fact, their somewhat stylized curves indicate that tailing under these conditions was negligible. The rising temperature technique will be discussed further in Chapters 7 and 11.

PHYSICAL CHARACTERISTICS OF THE STATIONARY PHASE IN GAS-LIQUID CHROMATOGRAPHY

Solid Support. When used as a support for a liquid, the solid material in the column should have large interconnected pores which provide minimum hindrance to diffusion. Such materials have low surface area, perhaps less than 20 m^2/g. Like the adsorbents, the supports should have reasonable particle size and chemical inertness. Diatomaceous earths such as Celite, and their derived products such as crushed insulating brick, are almost universally used. As one exception, Ellis and Iveson (569) used Teflon or Kel-F particles impregnated with liquid poly(trifluoro-

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monochloroethylene) as a solvent for analyzing blends of chlorine and fluorine and their compounds. Various workers have used a commercial detergent as a combination support and liquid phase.

Liquid Phase. The solvents themselves are normally nonvolatile, chemically inert liquids. As the temperature is raised decomposition becomes more likely, and the solvent itself is lost at a rate depending on its vapor pressure. Whitham (556) found that DC-710 silicone gave off benzene at 250°C when coated on Sterchamol, a European insulating brick.

As a first approach to setting a vapor pressure limit, Burrell Bulletin 835 suggests 0.01 or at the most 0.1 mm mercury (352). Keulemans (439) gives proposed maximum operating temperatures for various solvents. Table 5-1 contains some of the available suggested limits from these and other sources.

TABLE 5-1. SUGGESTED MAXIMUM TEMPERATURES FOR VARIOUS GLC SOLVENTS, °C.

Dimethylformamide	20
Dimethylsulfolane	25
Diglycerol	100
Polyglycols	100
Carbowax 1000	180
Dinonyl phthalate	140
Squalane	140
DC-710 silicone	250
Bitumen	250
Apiezon L	250
Asphaltenes	320
High Vacuum Silicone Grease	350

A little familiarity with these solvents shows that none suitable for operation at 200°C or higher is polar, when compared with diglycerol or dimethylformamide. Since high boiling samples are also relatively nonpolar, solvent effects tend to be weak where they are most needed because of the multiplicity of isomers.

The result is a tendency to stretch the ideal limits

a little. What happens then? In the first place some solvent will be lost. More will probably be lost from high solvent concentration columns than from low, because volatility of thin films is reduced somewhat by adsorption. If the vapor pressure is 1 mm the loss will be some 0.1 gram per day from a 1/4 in. column. Most of this will come from the first part of the column, where the support may become dry. Dry supports affect peak times and shapes (Chapter 7). In the less extreme case the retention volumes will be reduced, but the relative times will not be changed. Taylor and Dunlop (505) used a dimethylformamide column until it became noticeably worse from the standpoint of separation efficiency before replacing it (Fig. 5-4). They disregarded small changes in absolute times which did not affect the analysis.

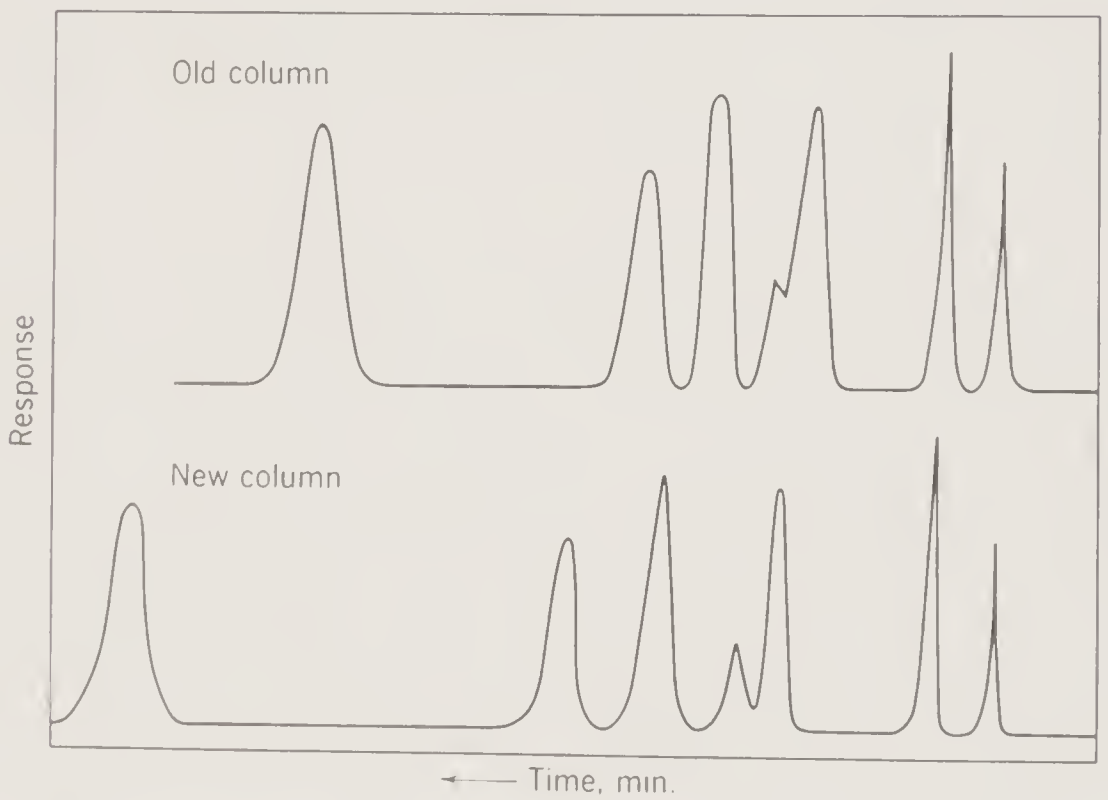

Fig. 5-4. Separation of hydrocarbons on old and new columns. Courtesy of Instrument Society of America (551).

To a large extent, the solvent level on the column can be maintained by saturating the carrier at column temperature before it enters the apparatus. By this technique Kwantes and Rijnders (606) were able to pass a compound over a solvent consisting of the next higher member of the same homologous series. This work was discussed in Chapter 3.

Another problem with volatile solvents is condensation in cooler parts of the apparatus. A droplet of solvent

bubbling in a restriction will change the carrier flow, and wreak havoc with an otherwise suitable baseline. If the detector is non-flow-sensitive, a solvent droplet in the cell chamber may still affect the response. Such condensation will surely occur in the trap used to collect samples, and affect any further analysis.

Finally, the amount of solvent in the carrier will vary with column temperature, causing baseline drift (long term change) or even noise (short term change) if the temperature control is poor.

The problem of solvent evaporation is most severe with industrial apparatus designed to read out in the form of a bar graph, where each peak is timed. Any change in column characteristics can force frequent readjustment of the controls.

There are two entirely different stationary phases not touched on before. One is the capillary tubing wetted-wall column of Golay (395, 577) where the inside of the tube serves as the support.

Combustors. The other type of "stationary phase" is a hot copper oxide bed used to oxidize the sample, as discussed for example by Norem (468). Some advantages of oxidizing the sample are as follows. The detector can be operated at low temperature, particularly if the water is removed on a drying column, as is usually the case. Maximum sensitivity can be achieved with katharometer detectors, because the temperature difference between the sensing element and the carrier can be a maximum. Then too, carbon dioxide derived from a hydrocarbon weighs more than the hydrocarbon, and thermal conductivity detectors are sensitive to weight. Finally, the recorded curve will be entirely on a carbon dioxide basis, so no calibration factors will be needed to correct the areas for varying detector response to different materials.

Disadvantages are that the components must be known in order to calculate the results. For example, methyl alcohol will appear as one carbon but ethane will appear as two, and so on. Identification of the components by trapping is impossible without equipment alterations. Difficulties with less common elements can be envisioned, such as poisoning the oxidant and complicating the area interpreta-

tion. Without the oxidation step no calibration factors need be used as a first approximation, with helium or hydrogen carrier. The added equipment undoubtedly reduces the efficiency somewhat by adding to opportunities for diffusion.

Chapter 6

COLUMN CONDITIONS

H. S. Knight

Shell Development Company

EFFECT ON EFFICIENCY

EFFICIENCY MEANS the ability of the column to produce narrow peaks, which will be adequately resolved even though the peak maxima are not separated very far in time. Efficiency is measured in theoretical plates, where one plate corresponds to one equilibrium stage in a stepwise separation. An equation for calculating plates from a GLC curve is as follows:

$$\text{No. of plates} = \underline{n} = \left(\frac{4\,V_R}{\Delta V}\right)^2$$

where V_R is the retention volume measured from the time of charging the sample and ΔV is the extrapolated peak width in volume units. Both may be measured in distance on the chart. (Compare with equation 2-1). Actually separation is a continuous process and plates are just a mathematical convenience, already familiar to many through the analogy with packed columns in distillation.

Van Deemter Equation. An equation for predicting efficiency, derived from considerations of GLC as a continuous process, is due to van Deemter et al. (316). This equation gathers the important variables contributing

to efficiency together and shows the approximate effect of each. Some supporting data have been given by De Wet and Pretorius (559) and some contrary data are discussed later. The equation yields HETP, the height equivalent to a theoretical plate, or the length of column corresponding to one equilibrium stage. It is usually expressed in centimeters.

$$HETP = 2\lambda \underline{d_p} + 2 \frac{\gamma D_{gas}}{\underline{u}} + \frac{8 \underline{k'}}{\pi^2 (1 + \underline{k'})^2} \cdot \frac{\underline{d_f}^2}{D_{liq}} \underline{u}$$

This is often reduced for discussion purposes to:

$$HETP = A + B/\underline{u} + C\underline{u}$$

The effects of operating conditions on HETP have already been mentioned in Chapter 2, and will be reviewed here. We will discuss the equation in terms of A, B, and C, referring back to the original for the makeup of these constants.

The A term is made up of two factors, λ and $\underline{d_p}$, representing packing irregularity and particle diameter. A large packing irregularity and a small particle diameter counterbalance. For example, unsized Celite particles are very small but columns made from them are not as efficient as those made from coarser grades. It is considered that the fine particles do not pack well enough. The A term is independent of linear velocity, $\underline{u}$.

The $B/\underline{u}$ term disappears at high velocity. The diffusion in the gas phase, D_{gas}, is reduced owing to lack of time. The γ is the packing tortuosity factor.

The $C\underline{u}$ term becomes larger at higher velocity. It represents the degree of equilibrium attainment during the separation. $\underline{k'}$ is a measure of the ratio of solute in the liquid to solute in the gas phase. Good solvents result in high values for $\underline{k'}$ giving better efficiency. The film depth, $\underline{d_f}$, appears as the square. D_{liq} is the diffusion in the liquid phase. At high velocity this will limit equilibrium attainment.

The effect of temperature on efficiency is not explicitly covered by the van Deemter equation, but temperature enters in through the diffusion terms and $\underline{k'}$. As temperature increases, D_{gas} and D_{liq} increase, having opposite

effects on HETP. The value of $\underline{k}'$ will decrease as more solute will be forced into the gas phase, decreasing the efficiency. The net effect will depend on the magnitude of all these changes.

The effect of liquid film depth may be seen by reference to the $C\underline{u}$ term. The depth itself occurs as the square, but thicker films increase the amount of solute in the liquid phase as represented by $\underline{k}'$, and hence the effect is less marked than otherwise.

The equation may be plotted as in Fig. 6-1. It is shown that there is an optimum linear velocity.

The data necessary to calculate HETP from the equation will in general not be available. All of the practical variables have been studied empirically by various workers, and some of their results will be discussed next.

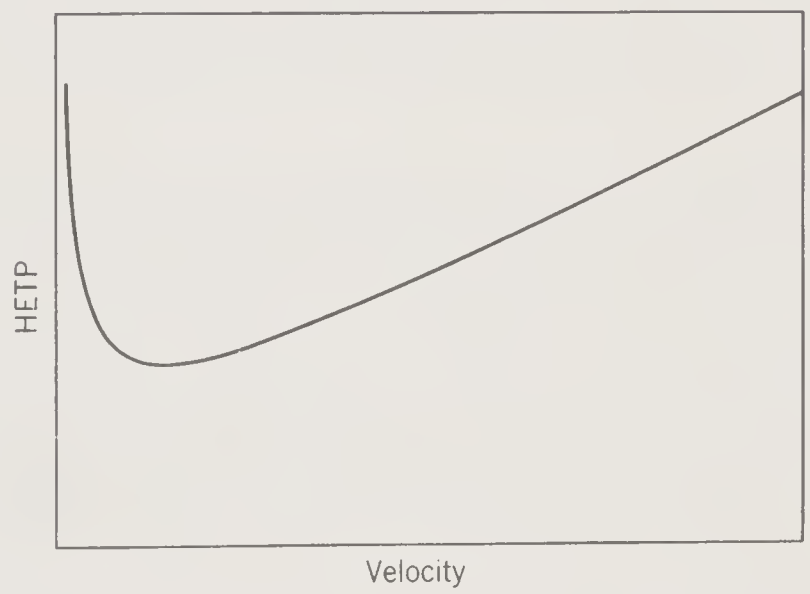

Fig. 6-1. Plot of the van Deemter equation.

Experimental Verification of the van Deemter Equation. Rangel (296) investigated the effect of temperature using propane solute over kerosine solvent. He concluded that the lower the temperature the better, down to the freezing point of the solvent. The writer believes that this will not be true of viscous solvents like glycols, with which D_{liq} will increase rapidly with increasing temperature.

Cheshire and Scott (549) studied the effect of particle size on column efficiency. They concluded that finer particles led to higher efficiency, at least up to 120-160 mesh. A wide range fraction, 100-200 mesh, was inferior to the 100-120 material (Fig. 6-2). They settled on 100-120

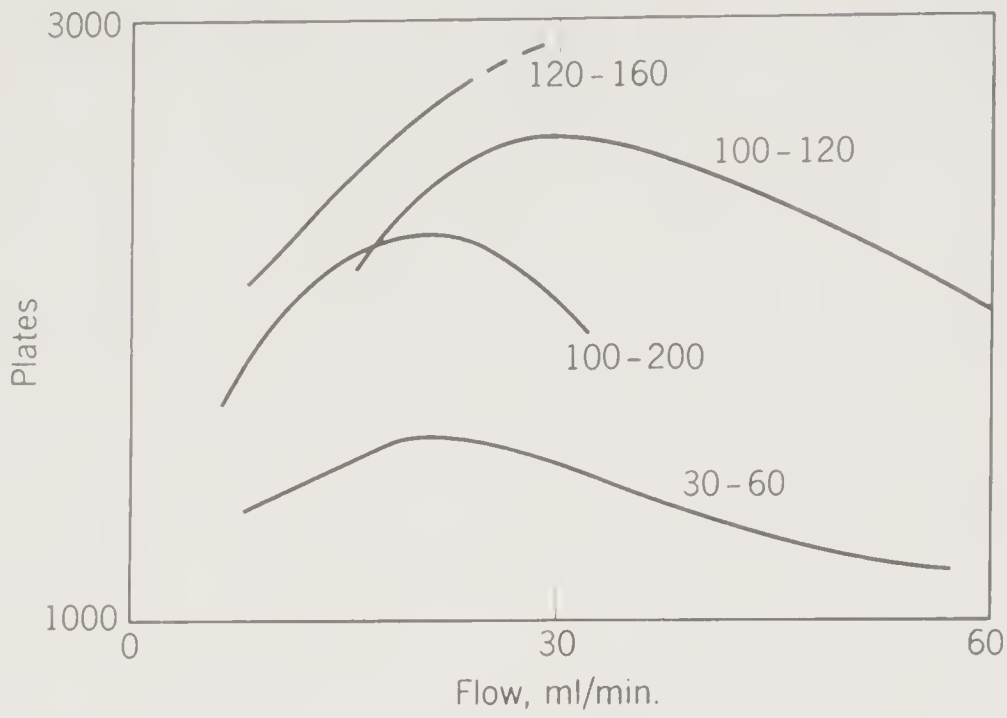

Fig. 6-2. Number of plates as a function of flow rate and particle size. After Cheshire and Scott (549).

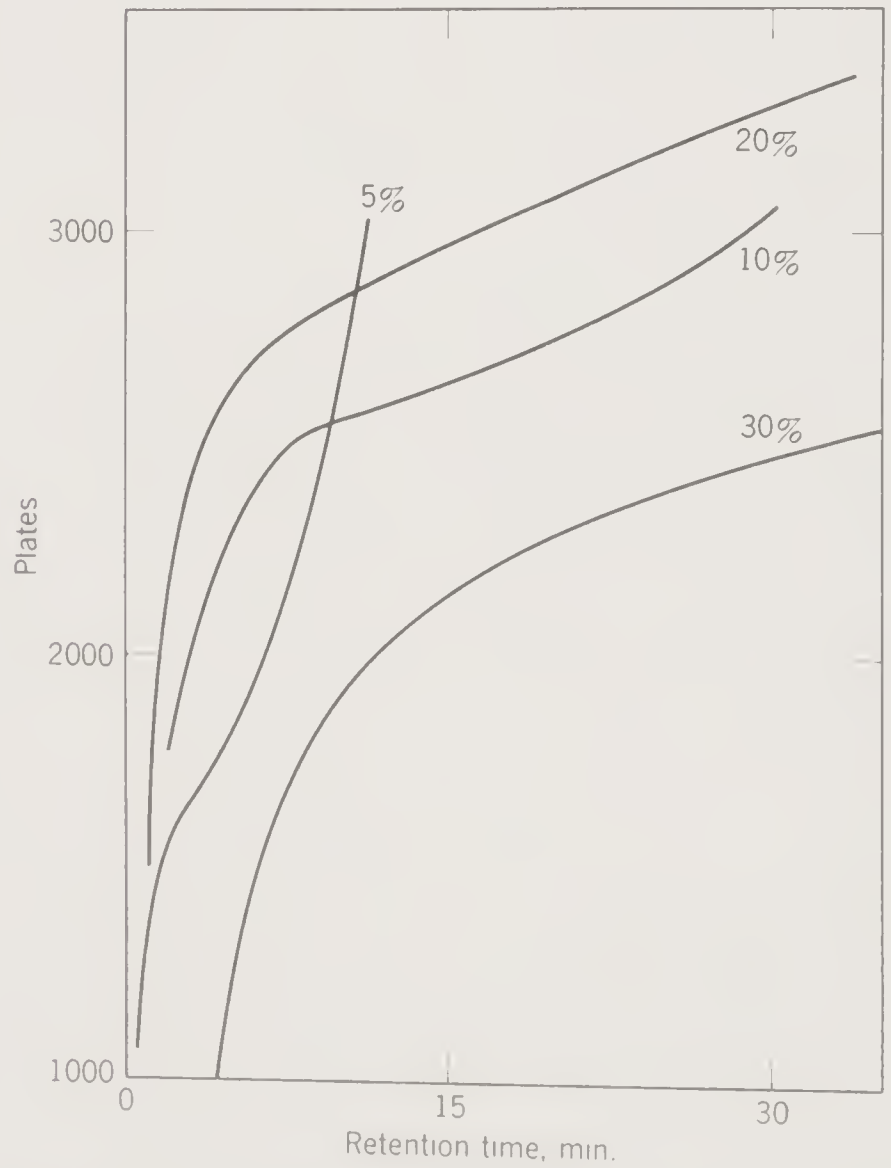

Fig. 6-3. Plate efficiency as affected by solvent concentration and retention time. After Cheshire and Scott (549).

mesh as optimum in glass equipment, as the fine particles produced dangerously high pressures at the optimum flow rate. These workers also studied the effects of the concentration of liquid phase on the support, and of retention time, on efficiency. The results are shown in summary form in Fig. 6-3. The curves rise steeply with increasing retention time, then become linear, except for the 5% solvent case. The highest boiling component of the hydrocarbon test mixture emerged in about 10 min at the low solvent concentration. The curve had not become linear at that time. The authors interpret the general shapes of the curves in terms of the van Deemter equation.

Cheshire and Scott recommended long columns of 5% solvent (5 parts per 100 of support) for low boiling samples. The long column retards them sufficiently for good separation. Shorter columns are recommended for high boiling materials, to reduce analytical time. Based on these principles, they made a 25 ft. column of 5% Apiezon L solvent on 60-100 mesh support (even 100-120 was too fine for this long column in glass equipment) to compare with the above 5 ft. columns. With 0.4 mg samples they obtained 10,000 or more plates.

In this work, Cheshire and Scott claimed that with their conditions plate efficiency was proportional to column length for the first time.. Later Scott (640) made a 50 ft. column and found its efficiency to be considerably less than twice that of the above 25 ft. column. He attributed the discrepancy to the large ratio of inlet to outlet pressure, with its accompanying large velocity gradient. It was impossible to operate the column at close to the optimum velocity throughout.

To reduce the pressure ratio while still providing adequate pressure drop to move the carrier gas, he converted to metal equipment and operated the entire assembly under pressure. With 200 psi inlet and the outlet restricted to give optimum flow the column had 30,000 plates, for an HETP of less than 0.06 cm. He used a special charging technique to place the sample on the column.

Bohemon and Purnell (540) have also studied the effects of particle size on column efficiency. They used a 120 cm column of 20% polyethylene glycol solvent and nitrogen carrier. Their detector consisted of a single thermal

conductivity filament. They blended 30-40 and 50-60 mesh crushed brick and obtained worse results until the blend was more than half fine grade. Again, the narrow range support was preferable. With 100-120 mesh support and nitrogen carrier they obtained 1400 plates per ft. for an HETP of 0.05 cm. They found that as sample size was decreased the efficiency increased (Fig. 6-4). The effect was most marked for isopropyl alcohol, less so for hydrocarbons and acetone.

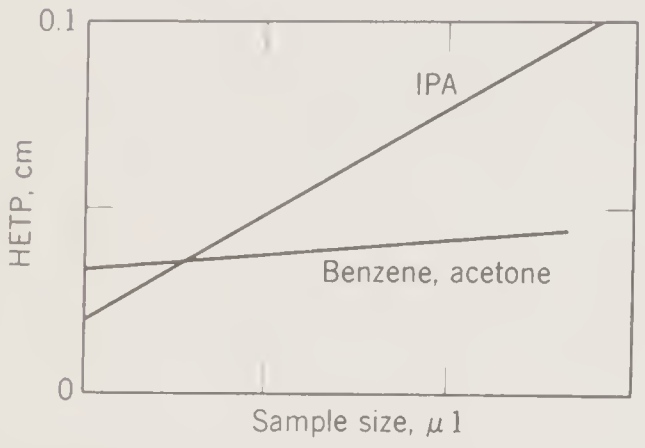

Fig. 6-4. Effect of sample size on column efficiency. After Bohemon and Purnell (540).

In interpreting their results they used the simplified version of the van Deemter equation, and recognized the possibility that the A, B and C constants might not be composed of the same terms as shown by van Deemter. For example, A was often negative, and B varied erratically with particle size.

They calculated that at 4 atm average pressure the above column would have 2000 plates per ft.

It may be that the HETP's reported above were limited by equipment factors. If the sample is charged over a long time period, the peak will be wide. The problem is to add the sample as a sharp slug and have it dissolve in the shortest possible length of column. Indeed, the advantage of small samples is they can be added instantaneously and are immediately absorbed on the first short section of column. In this view, still smaller samples ought to be still better if they could be added effectively.

Effective efficiency seems to improve if the temperature is raised continuously during the analysis. An example was given earlier for the GSC case, in which Greene and Pust worked with hydrocarbons through C_4. Dal Nogare and Bennett (624) separated the alcohols from methyl to nonyl by such a technique (Fig. 6-5). The curve shows evenly spaced, symmetrical peaks on the silicone solvent (see Chapter 7). Analytical time was greatly reduced.

The foregoing sections of this chapter have covered the effects of the key variables on column efficiency.

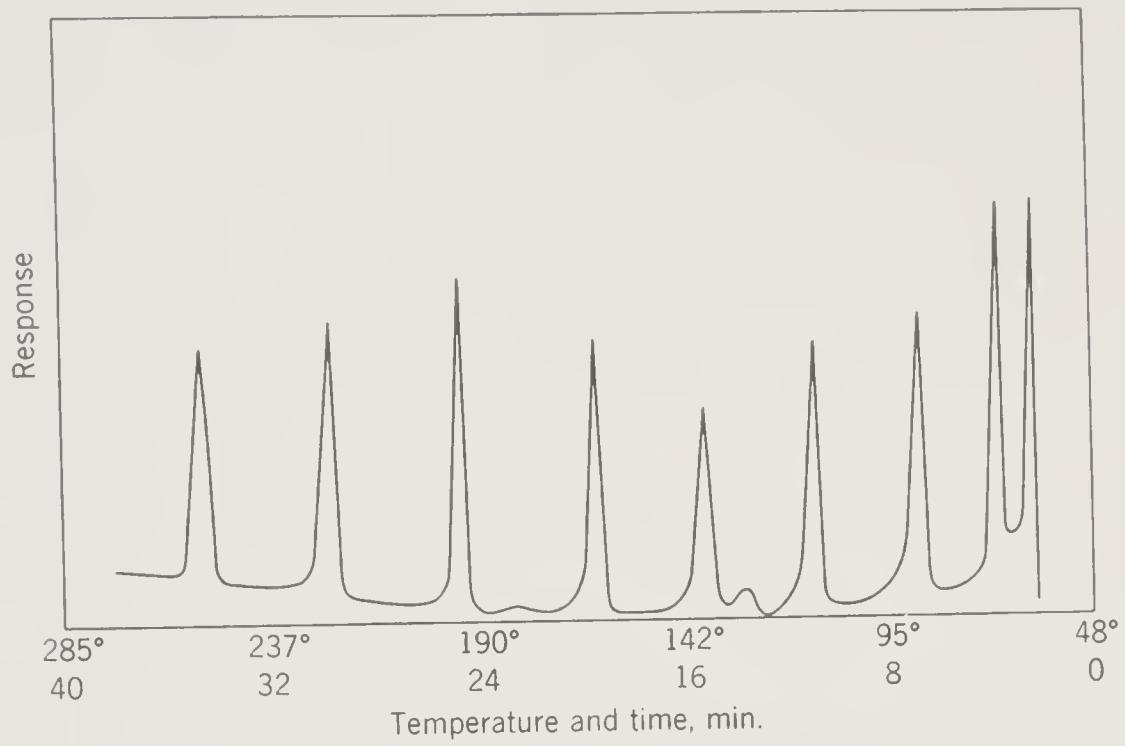

Fig. 6-5. Effect of temperature programming on peak shape. Courtesy of Analytical Chemistry (624).

Other effects of these variables which will be discussed in more detail later will be mentioned briefly here.

EFFECT ON PEAK SHAPE

Temperature affects peak shape by changing the extent of solvent-solute interaction. The required operating temperature restricts the choice of solvents to those that are not too volatile, unstable, or high melting. Temperature affects retention times, relatively and on an absolute basis. High temperature has a definite and deleterious effect on selectivity, or the ability of the column to separate materials according to type. Film depth affects the degree to which solute molecules are adsorbed on the surface of the support, which also affects peak shape.

Chapter 7

PEAK DISTORTIONS

H. S. Knight

Shell Development Company

DISTORTED PEAKS are undesirable for several reasons. They are broad at the base, causing overlapping of adjacent peaks. The retention time of the peak, which is normally measured to the peak maximum, varies with sample size. The area is indeterminate if the curve approaches the base-line asymptotically. Finally, the area of a peak superimposed on the slope of another cannot be integrated automatically.

CAUSES OF DISTORTION

Distorted peaks result when a changes with solute concentration, in other words, when the "sorption" isotherm (including adsorption and absorption) is nonlinear. The usual GLC curve is Gaussian, with the tips of the base representing the minimum concentration of solute. If the isotherm is such that small amounts of material are disproportionately held, a will be low at minimum concentration and the tips will be retarded. The front of the peak will merge with the bulk of the peak, causing a straight leading edge, and the rear of the curve will be elongated, causing tailing. If a is high at infinite dilution, the rear of the peak will be straight, and the front elongated. This is called leading.

In either leading or tailing, the emergence time

of the distorted peak tip depends on the a value at infinite dilution. The emergence time of the tip is therefore constant. A very small sample would emerge at that time. As larger samples are added the bulk of the peak will deviate more and more from the tip.

In GSC, adsorption is the only possible source of a nonlinear isotherm. In the great majority of adsorption studies, the isotherm is similar to the one shown in Fig. 7-1. Here small amounts of solute are very tightly held. Tailing is to be expected, and tailing is observed except with fixed gases, unless special precautions are taken. Gregg and Stock (581) were able to find GSC systems representing various types of isotherms and to show that the peak shape could be predicted from the isotherm in the way discussed here.

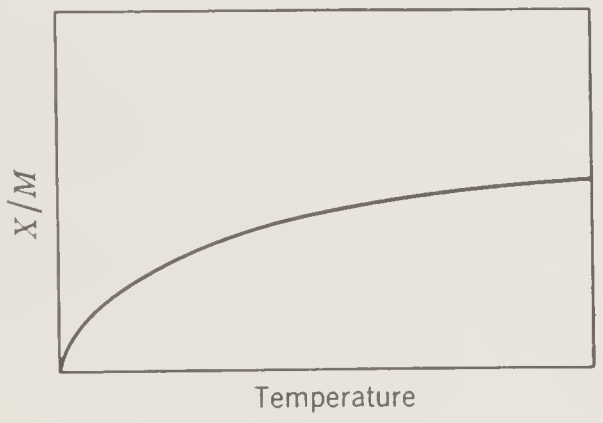

Fig. 7-1. Typical adsorption isotherm.

REDUCTION OF DISTORTION

One cure for tailing in GSC is the use of a displacement technique. For example, the carrier can be saturated with benzene, which will displace saturates and prevent them from tailing. A difficulty here is that the column is left saturated with benzene and must be regenerated prior to reuse. Another difficulty is that the displaced components emerge successively, and are not separated by carrier. Usual detection methods are not applicable unless the successive components differ in the property being detected. Markers might be found to show the zone boundaries, but this complicates the situation very seriously.

Modification of Surface. Since adsorption is a surface phenomenon it should be possible to reduce the surface or to change its nature to reduce adsorption. Minimum surface is presented by glass beads, which still cause tailing. Reacting polar surfaces with chlorosilanes failed to eliminate peak distortion (604).

White and Cowan (657) were able to make an adsorbent with a linear adsorption isotherm for certain samples by reacting the exchangeable groups in a swelling bentonite with an organic amine. They calculated the amine chain length to just cover the surface while using all the exchange capacity of the clay. A commercial product, Bentone 34 (National Lead) was found to approximate their specifications. This material gave symmetrical peaks. They obtained an HETP of 0.05 cm.

DISTORTION IN GLC

In GLC the $\underline{a}$ values could vary with concentration either because of adsorption or solution effects. As outlined above, tailing goes with a low activity at low concentration, which could occur as a result of a non-ideal solution in which γ goes down with concentration. Such low γ values result from complex formation or from differences in molecular size. Complex formation is not very common, and molecular size differences have not caused tailing in practice. For example, pentanes do not tail with squalane ($C_{30}H_{62}$) columns. Therefore, it is felt that tailing in GLC is almost always caused by adsorption.

Polar materials tail more than nonpolar ones because they are more strongly adsorbed on the common polar supports. Liquid phase data are evidence for the statement that polar materials are more strongly adsorbed in GLC. Other evidence is obtained by comparing activity coefficients from vapor-liquid equilibrium with those from GLC. Kwantes and Rijnders (606) found noticeable discrepancies unless nonpolar solutes were employed. Still further evidence is available from GLC data showing that relative retention times vary as the solvent concentration changes. This must be attributed to adsorption. Eggertsen et al. (209, 566, 567) found that not even hydrocarbons are immune to relative time shifts with solvent concentration. These data will be discussed later. Knight (604) found that even with polar solvents the new high efficiency columns are susceptible to solute adsorption. Some data for triethylene glycol solvent are given in Table 7-1, based on an assigned $\underline{a}$ value of unity for methyl alcohol.

TABLE 7-1. SOLVENT CONCENTRATION AND RELATIVE a VALUES

Triethylene Glycol, %	MeOH	n-BuOH	Ethyl Acetate	n-Hexane
1	1.00	1.9	3.5	10
3	1.00	2.7	4.8	26
10	1.00	2.6	5.4	55

In efforts to control tailing, many of the same techniques cited above for the GSC case have been studied. Dal Nogare and Bennett (624) obtained symmetrical peaks for alcohols by increasing the temperature during the analysis. The volatility of the material represented by the tail was increased, reducing the tail. Bayer (533) converted strongly adsorbed amino acids into more tractable materials by esterifying the acid and converting the amine to the N-trifluoroacetyl derivative.

Modification of Surface. By way of changing the nature of the support surface, Johns (433) added small amounts of fatty acids to the regular phthalate ester solvent and found that the C-22 insulating brick responded favorably to the treatment. Chromosorb (Johns-Manville) was less responsive but was inherently better than C-22, and was about as good as the treated C-22. Knight (604) found just the reverse, that C-22 was better than Chromosorb and was less susceptible to treatment with fatty acid. Desty (558) found that Celite was better than C-22 from the standpoint of tailing, but was stickier and harder to pack.

Dintenfass (373) studied the effect of an adsorbed material on the capacity of the adsorbent for another material of the same or a different type. He observed that one acid on the surface used the capacity of the adsorbent for acids, but not for other types of materials. In line with this finding, it should be possible to prevent tailing of alcohols by using a polyol solvent, but amines for example would still tail unless an amine were also added. In practice use of any particular solvent type is inconsistent with having available a wide variety of solvents.

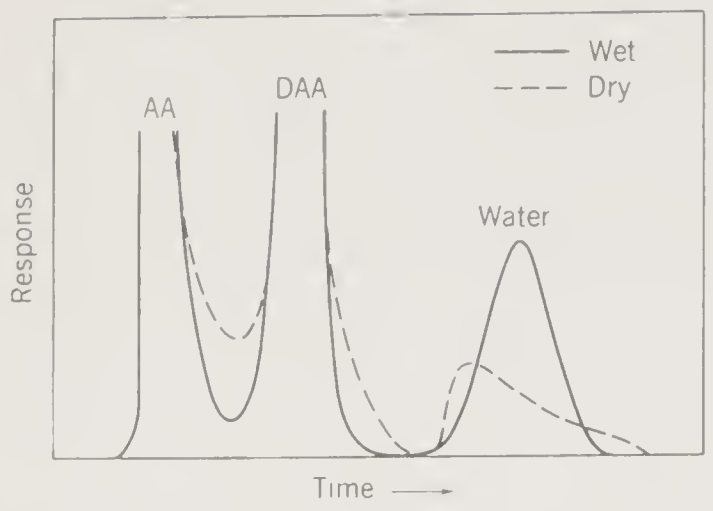

Fig. 7-2. Tailing is reduced by satiating the surface. Courtesy of Analytical Chemistry (604).

Modification of Carrier. The hydrocarbon case is easily solved, for any solvent seems to prevent tailing of these nonpolar materials. For the more polar samples, Knight (604) found that it was possible to reduce tailing by adding a volatile material, similar in type to the sample, continuously with the carrier. Solvent selectivity was little affected by the volatile tailing reducer. The carrier was saturated with the added material at room temperature, and very little of the tailing reducer remained on the column at the common operating temperature of 60°C. Nevertheless, the surface of the support was satiated for the particular type of material and the curved portion of the adsorption isotherm was avoided to a large extent. More symmetrical peaks were the result.

Fig. 7-2 shows the effect of adding water and an amine to the carrier on the shape of water and amine peaks. The carrier was saturated at room temperature with water and n-hexylamine and the column (mixed solvent, see Chapter 8) was operated at 60°C. With hydroxyl-containing solvents the effect on the water peak was less marked, while with nonpolar solvents the effect was greater. For example, analysis of a blend of four alcohols, methyl through n-butyl, was impossible on a hydrocarbon solvent without water in the carrier, at constant column temperature. While the rising temperature technique solves this particular problem it would be more difficult to apply if the

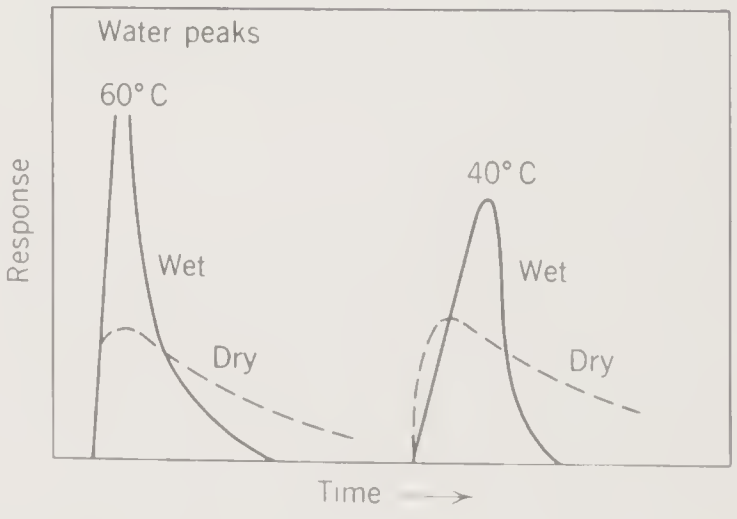

Fig. 7-3. Leading is reduced by raising the temperature. Courtesy of Analytical Chemistry (604).

sample was not a clean homologous series, but contained close boiling isomers which might be fused into a single peak.

Fig. 7-3 illustrates the effect of temperature on peak shape. At 40°C the water peak with wet helium has a sloping forward edge, which is called leading. Elongation of the forward edge is a solution effect, which in this case results in a high at minimum concentration. This type of non-ideality occurs when the solvent and solute differ in functional group. It is common in GLC. In severe cases the tips of the normal curve move ahead, causing the rear of the peak to be more vertical and the front to be elongated. In Fig. 7-3 leading and tailing are both apparent.

Note that leading is decreased by raising the column temperature from 40 to 60°C. Solutions tend to be more nearly ideal at higher temperatures, reducing the change in with concentration.

Experience has shown that most common volatile polar compounds can be analyzed by GLC at 60°C with a tailing reducer to give fairly symmetrical peaks. Close control of column temperature is necessary since the amount of volatile material on the column at equilibrium will otherwise change, affecting the baseline.

The foregoing discussion of tailing has neglected the mechanical cause, the method of introducing the sample. Porter et al. (292) showed that if the sample is introduced into a chamber from which it is swept exponentially into the column tailing will result. In well-designed equipment tailing from this source is minor. However, with high efficiency columns and sensitive detectors such tailing may cause trouble. It is essential to keep dead space in the apparatus to an absolute minimum for high efficiency. (See also Chapter 10.)

Chapter 8

COLUMN SELECTION

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Shell Devolopment Company

SELECTIVITY OF SOLVENT

CONTROL OF SELECTIVITY may make it possible to place peaks for one molecular type among peaks for other types with minimum overlapping. Fredericks and Brooks (213) found that dimethylsulfolane has enough polarity to retard olefins beyond the saturates of the same carbon number, without causing them to emerge with higher boiling saturates (Fig. 8-1). Less polar materials did not retard the olefins enough.

Desty and Whyman (368) studied the separation of C_4 to C_{10} hydrocarbons on n-hexatriacontane and benzyldiphenyl. Their data for saturates are reported in terms of carbon number, which means they are not corrected for the lower boiling points of isoparaffins compared to normal paraffins of the same carbon number. They show boiling point separation of types within one carbon number, with little difference between the two solvents for alkanes. The benzyldiphenyl retarded cyclics and aromatics on a type selectivity basis. They used the information to carry out a thorough analysis of fairly pure isooctane. A few sulfur compounds were also studied.

Eggertsen, Knight and Groennings (567) studied the separation of C_5-C_7 saturates on various substrates. They used 2,2-dimethylpentane and cyclohexane as a standard pair to show selectivity of the solvents for naphthene-

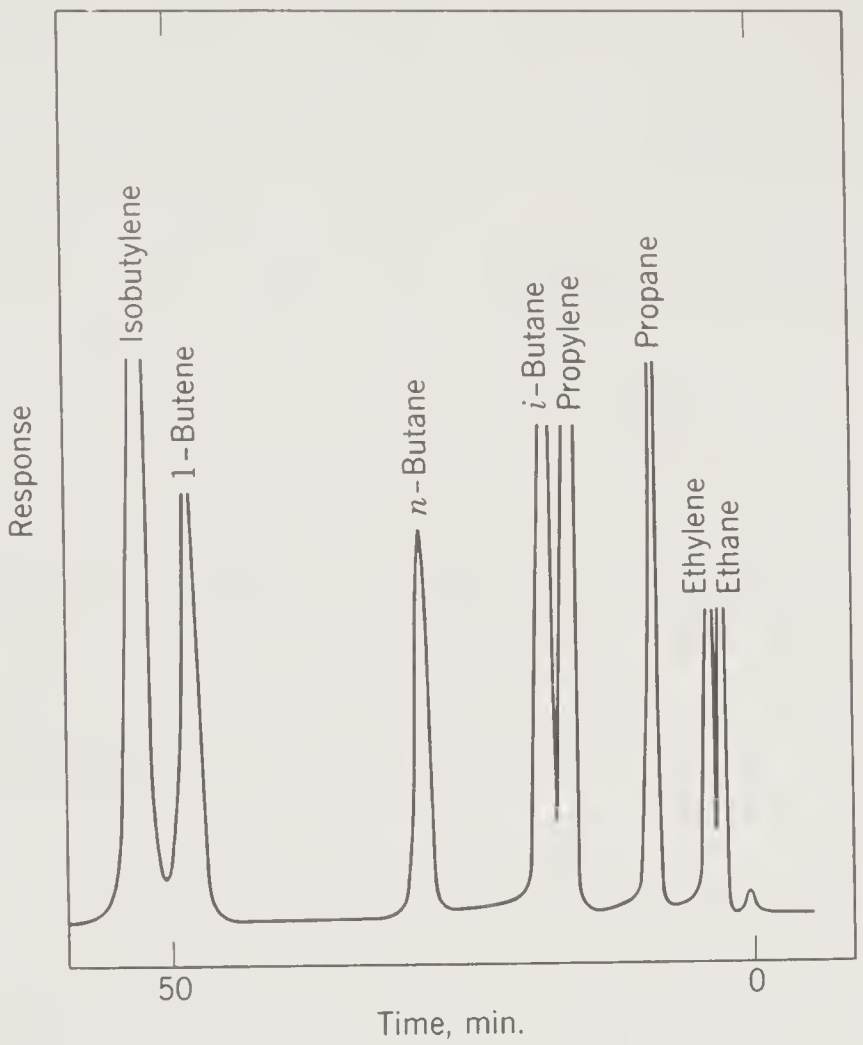


Fig. 8-1. Separation of light hydrocarbons. Courtesy of Analytical Chemistry (213).

paraffin separation. Since these compounds have the same vapor pressure, the retention time ratio, activity coefficient ratio, and relative volatility are all numerically the same. Table 8-1 gives some of the data.

TABLE 8-1. NAPHTHENE-PARAFFIN SELECTIVITY OF VARIOUS SOLVENTS

Solvent	Retention time ratio, cyclohexane to 2,2-dimethylpentane
Silicone SF-96	1.2
Squalane	1.4
Triethylene Glycol	1.8
Dimethylsulfolane	1.9
Ethylene Glycol	2.7
β,β'-Oxydipropionitrile	2.8

On all of these liquids the naphthene was retarded. SF-96 was the most neutral of these solvents. It was shown that the above data were typical of naphthenes and paraffins as classes (Fig. 8-2) even though 2,2-dimethylpentane could be regarded as an atypical paraffin. The cluster of points below the naphthene curve near the 90 min region represents the dimethylcyclopentanes, which are more paraffin-like as might be expected. The branched paraffins are not more naphthenic, in fact, Phillips (478) found that isooctane was less strongly held on a polar solvent than on a nonpolar one, compared to n-heptane.

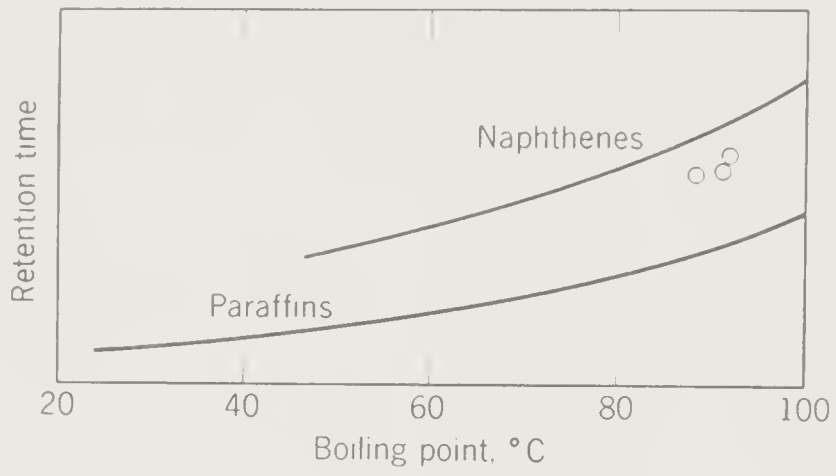


Fig. 8-2. Type separation on ethylene glycol. Courtesy of Analytical Chemistry (566).

The practical significance of the data in Table 8-1 is as follows. The naphthenes may be completely separated from the paraffins on the nitrile solvent if the highest vapor pressure of any component in the mixture is less than 2.8 times the lowest. The volatility of the highest boiling paraffin will then be greater than that of the lowest boiling naphthene.

Since practical mixtures may have greater volatility ranges than this, the above type separation by itself is inadequate. There are not too many naphthenes in the C_5-C_7 fraction, and it might be possible to make them appear in gaps among the paraffins. Actually the squalane solvent gave more individual peaks than the very polar columns.

AMOUNT OF SOLVENT

Eggertsen et al. studied the effect of amount of solvent on the support. Dry supports caused tailing, but

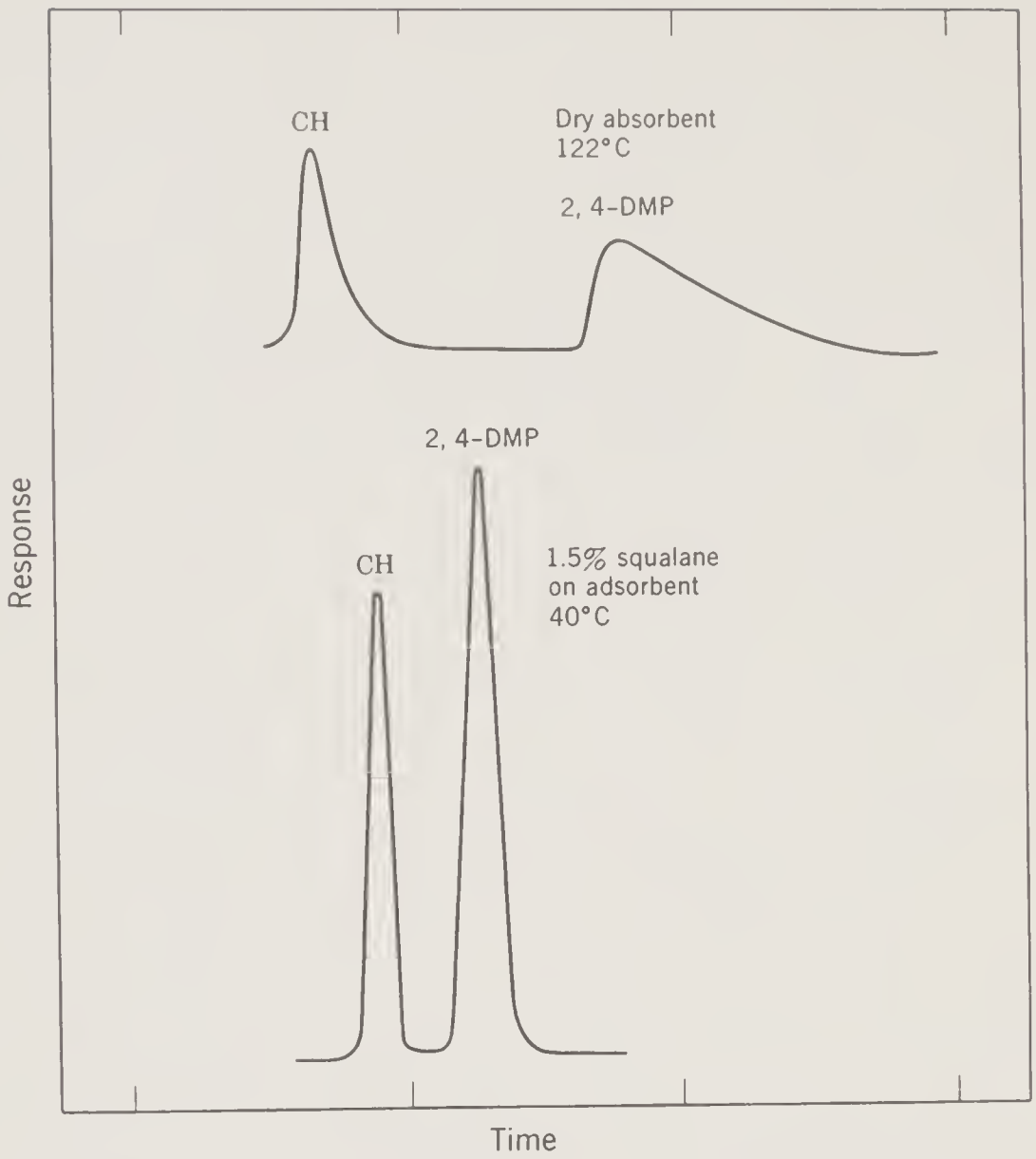


Fig. 8-3. Effect of solvent on peak shape. Courtesy of Analytical Chemistry. (566).

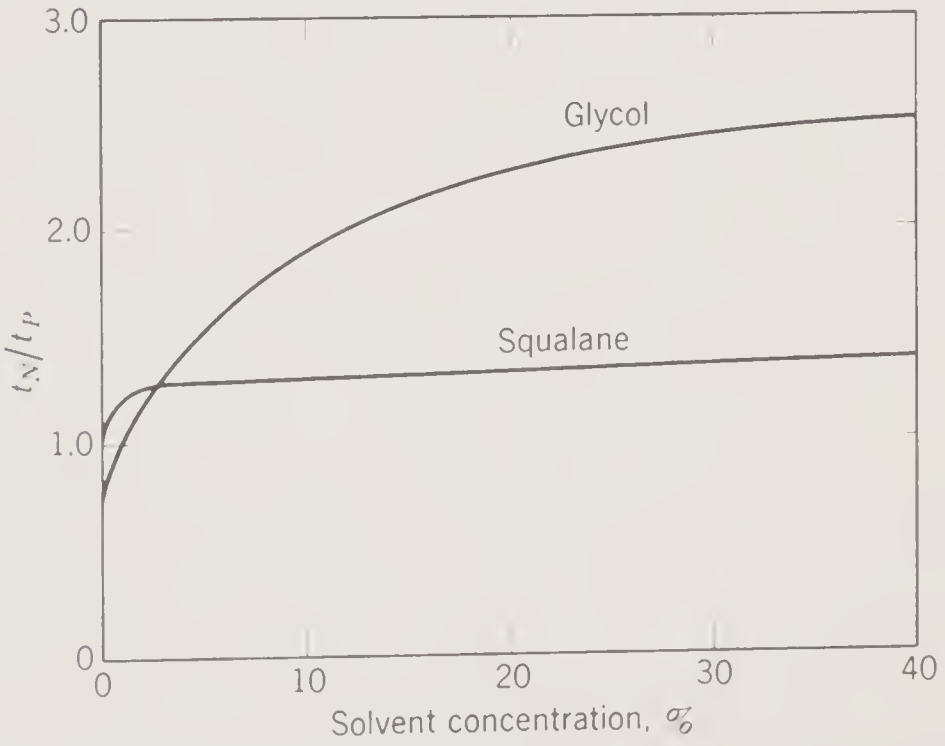


Fig. 8-4. Effect of solvent concentration on type separation. Courtesy of Analytical Chemistry (566).

were of interest because they retarded paraffins while all the solvents retarded naphthenes (Table 8-1). It was found that small amounts of solvent eliminated tailing (Fig. 8-3) without reversing the type sequence. As more solvent was added the naphthenes were retarded more and more, until the above liquid-type columns were the result (Fig. 8-4). There was a very useful intermediate stage where no type separation occurred (boiling point separation) and another where the naphthenes, which are higher boiling than the paraffins, emerged with paraffins of the same carbon number (Fig. 8-5). The carbon number column was useful for cutting out small amounts of lower and higher carbon number impurities in the C_5-C_7 fraction, and could be used to break up this fraction as a preliminary to complete type separation.

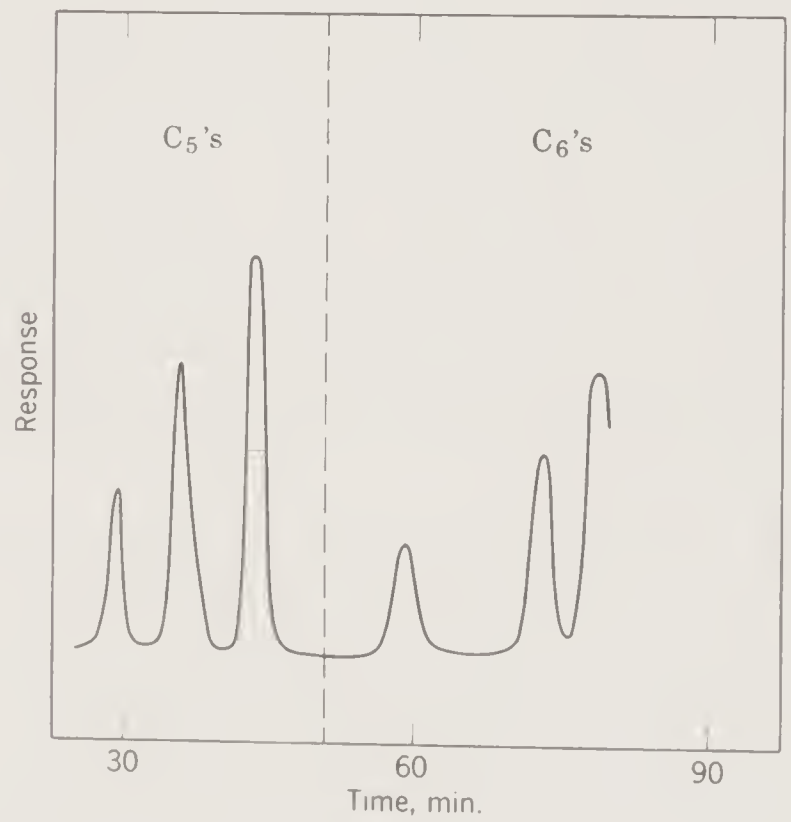


Fig. 8-5. Separation on "carbon number" column. Courtesy of Analytical Chemistry (566).

MULTIPLE COLUMNS

Another approach would be to separate a mixture on a paraffin-retarding column, trapping all of the naphthene-containing sequence. These materials could then be analyzed on a very polar column. The high boiling paraffins which would normally interfere with the type separation

would be absent. Thus the volatility range for complete type separation could be increased by about a factor of two (the relative volatility of cyclohexane to 2,2-dimethylpentane on the solid with tailing reducer is about 0.5).

Alternatively, the combined peaks from the squalane column (which gave the most individual peaks) could be trapped and analyzed by mass spectroscopy or on another GLC column.

Eggertsen and Groennings (567) used gas chromatography on three different columns to analyze a C_5-C_7 saturates blend. By combining the data from the three columns all of the compounds were determined except for 3-ethylpentane. Separation within the naphthene and paraffin spectra varied subtly from column to column to make the overall separation possible.

Zlatkis (664) and Tenney (649) have shown that perfluorotributylamine is similar to the solid adsorbents and different from most solvents in that it retards paraffins relative to naphthenes. Mixed columns of this and other solvents could be prepared to separate the types in various ways.

The separation of C_5-C_6 olefins was studied by Knight (603). This is an interesting system because so many types are possible, including mono- and diolefins, cyclic mono- and diolefins and acetylenes, although the latter were not included in the study.

The carbon number column mentioned above was suitable for olefins, although the exceptionally low-boiling isomers were probably included with the next lower carbon number if they were present at all. The carbon number column was used to isolate the C_5 and C_6 fractions.

Adsorption could not be ruled out so $\underline{a}$ values were reported rather than solvent-solute activity coefficients. An $\underline{a}$ value of unity was assigned to 1-hexene, and with this basis only the retention times and the vapor pressures were needed to calculate $\underline{a}$ values for other materials.

On polar solvents one double bond was equivalent to closing the ring in its effect on the $\underline{a}$ value. The effect of a double bond went down as the carbon number went up, as might be expected, since polarity decreases with increasing molecular weight. Data on the polar solvent, ethylene glycol, are given in Table 8-2.

TABLE 8-2. EFFECT OF STRUCTURE ON RELATIVE ACTIVITY COEFFICIENTS ON ETHYLENE GLYCOL

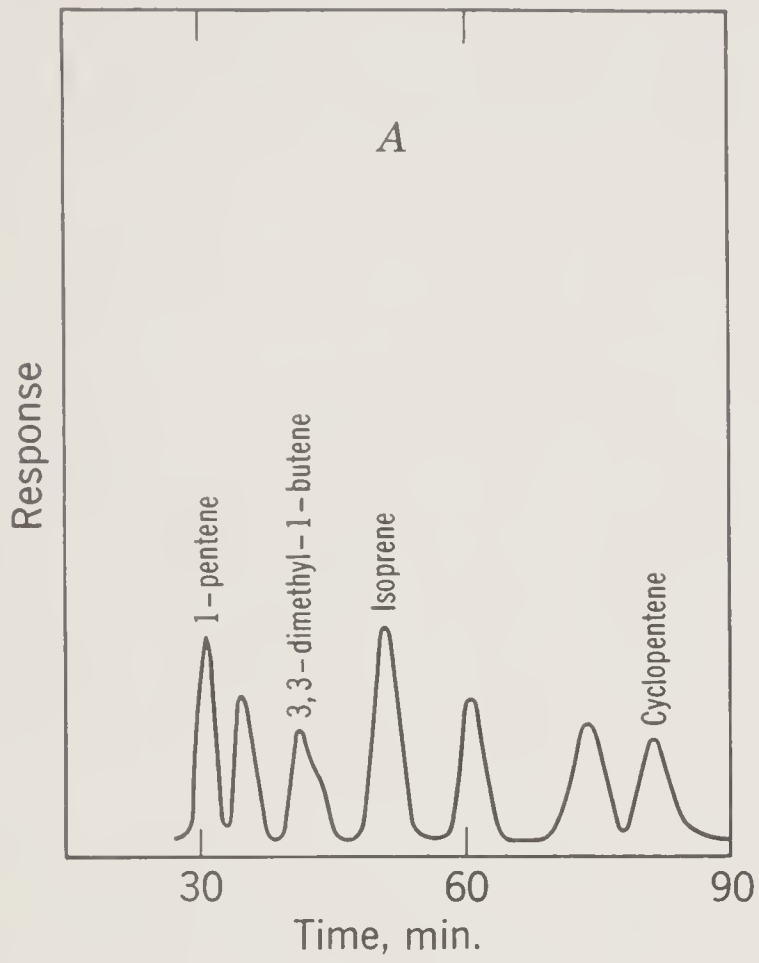
Compound	Relative a (1-hexene = 1)
n-Pentane	1.1
Cyclopentane	0.6
1-Pentene	0.5
Cyclopentene	0.25
2-Methyl-1,3-butadiene	0.2
n-Hexane	1.6
1-Hexene	1.0 (assigned)
Cyclohexene	0.5
Methylpentadienes (mixed)	0.5
Benzene	0.1

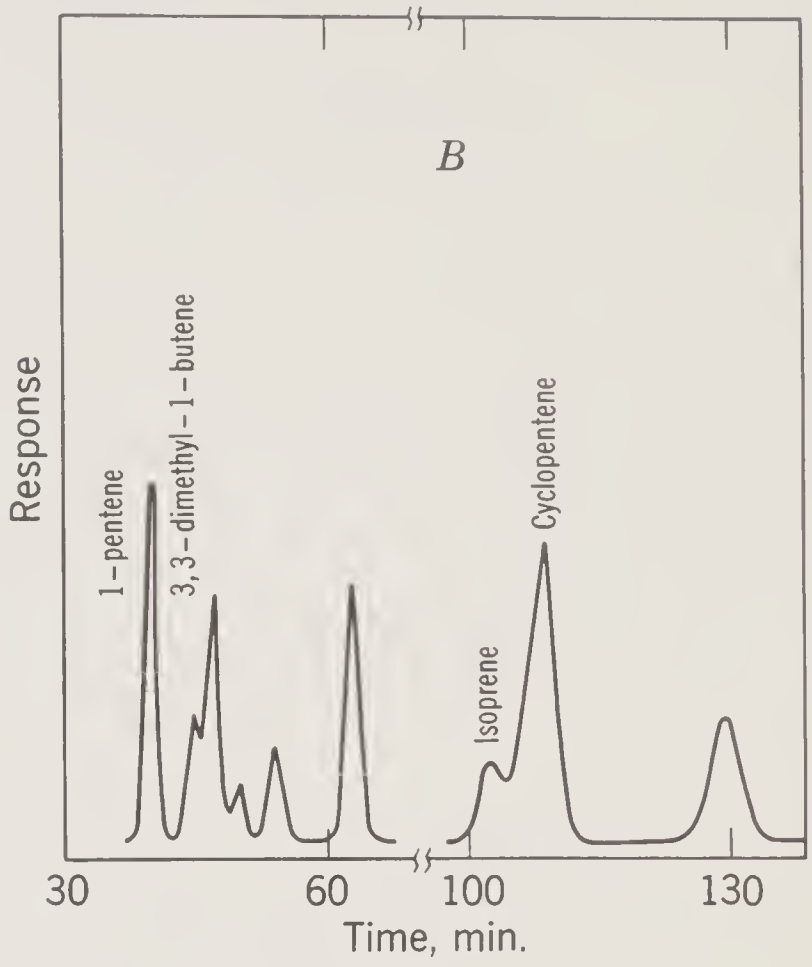
Thus the paraffins can be separated from the monoolefins and naphthenes of the same carbon number if the vapor pressure range covers somewhat less than a factor of two. The same is true of cycloolefins and alkenes. Aromatics can be separated from saturates over a range of 15. Note that the solvent is very sensitive to carbon number, with about a factor of two difference between C_5 and C_6. Cycloolefins and dienes which are together on the polar solvent can be separated on a nonpolar solvent which retards the cyclics.

EFFECT OF POLARITY

Illustrating the above data for the C_5's are Figs. 8-6, 7 and 8. These show the effect of increasing solvent polarity on the type separation. For example, the low boiling hexene, 3,3-dimethyl-1-butene, moves ahead as polarity increases, until on the nitrile solvent it emerges with 1-pentene. Its higher carbon number makes it more active on the polar solvent. Again a balance of selectivity is best, for the dimethylsulfolane provides the most useful separation. It places cyclopentene with 3-methyl-1,2-butadiene, which is not likely to be present.

The hexene separation was also studied, but is not described in detail here because no new principles are involved. It is of interest, however, that β,β'-oxydipropionitrile and dimethylsulfolane happen to form different sets





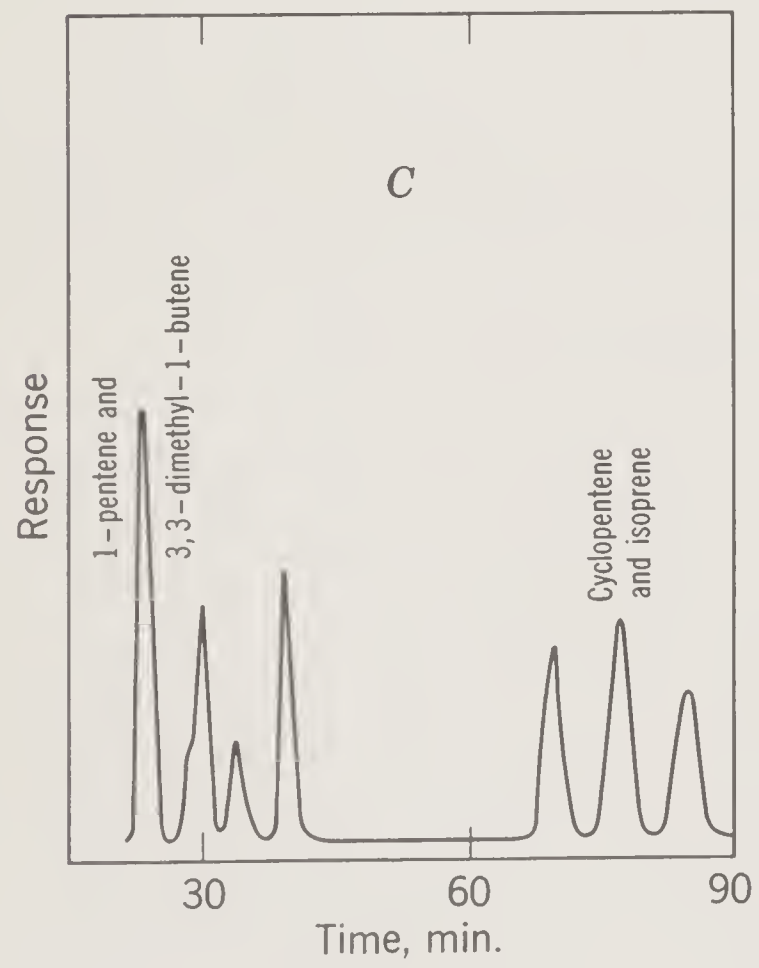


Fig. 8-6. Separation of pentenes on columns of increasing polarity:
A, slightly polar;
B, intermediate polarity;
C, very polar.

Courtesy of Analytical Chemistry (603).

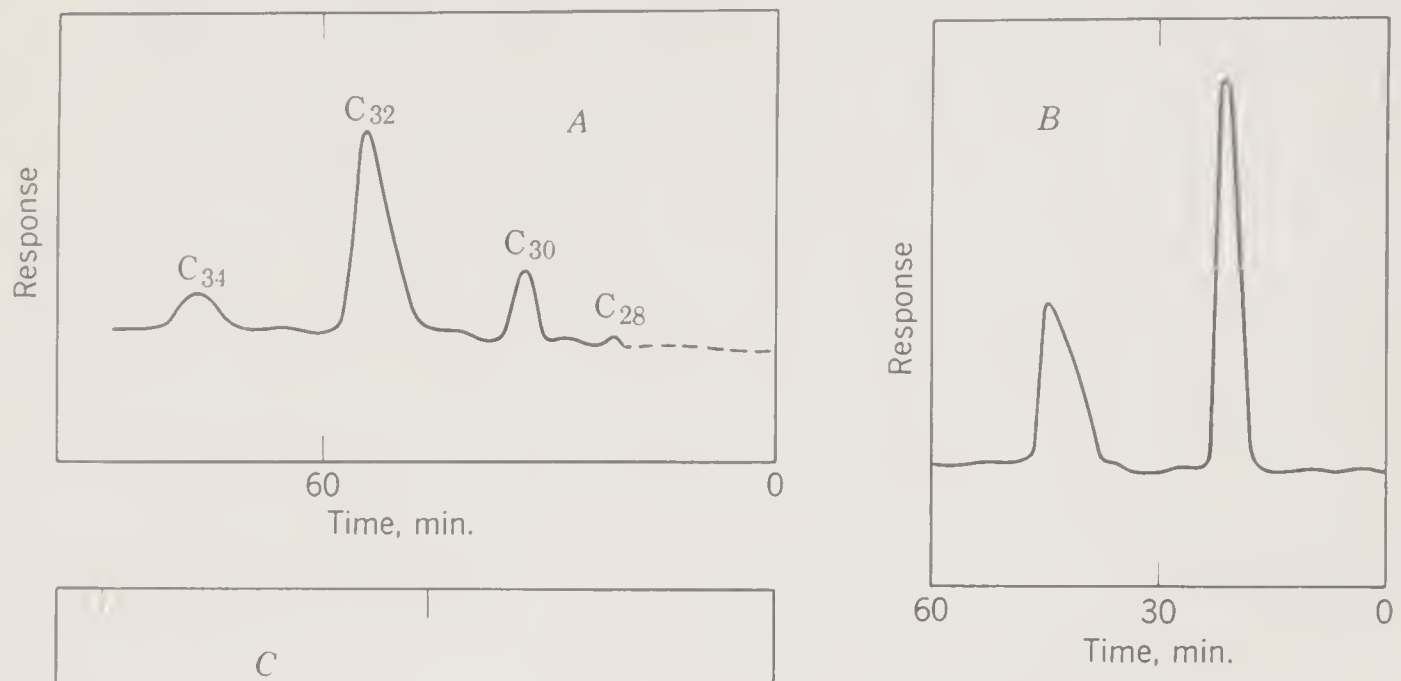


Fig. 8-7. High temperature separations: A, methyl esters at 290°C; B, benzyldiphenyl isomers at 200°C; C, crude wax at 290°C. After Adlard and Whitham (526).

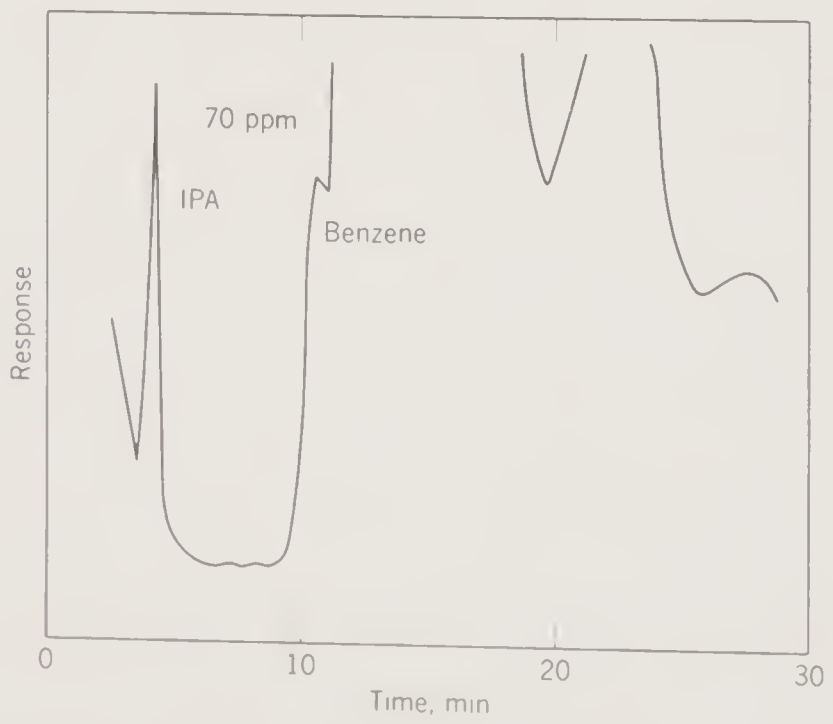


Fig. 8-8. Trace analysis with 100 microvolt full scale deflection. Courtesy of Analytical Chemistry (535).

of pairs among the monoolefins. By analyzing on both columns and combining the results, all the components are determined except for the pair, 3- and 4-methyl-1-pentene which did not separate on any column studied. These small, unpredictable but important shifts make it necessary to emphasize trial and error for selecting specific columns.

Published aromatics separations are in general of the boiling point type. Jones (435) separated aromatics through C_9 on Apiezon L at 297°F. It is of interest that at the time he was able to refer to his work as high temperature GLC. Desty and Whyman (368) included aromatics through the xylenes in their study of n-hexatriacontane and benzyldiphenyl. The aromatics were retarded fairly strongly on the more polar benzyldiphenyl compared to n-paraffins of the same carbon number.

Zlatkis, O'Brien and Scholly (664) separated m- and p-xylene on a column only five meters long. The conditions were as follows: 100°C, 60-80 mesh Chromosorb support, 15% benzyldiphenyl solvent, 59 psi inlet pressure, 100 ml/min flow of helium, 0.005 ml of sample. The column had 9,500 plates, and the separation was 20-30% complete.

In hydrocarbon analysis little work has been done on GLC of mixtures containing all types of hydrocarbons. The saturates, olefins and aromatics may be separated by liquid phase chromatography prior to the analysis, and the sample may be fractionated by GLC or distillation. However, the separation of saturates and aromatics by types is good enough to suggest application of GLC directly to straight run gasoline (649).

Much of this chapter is devoted to hydrocarbons because most of the published literature concerns hydrocarbons. Tenney (649) studied type separations for hydrocarbon and oxygenated compound systems. His paper is outstanding as a general source of practical GLC data. He presented plots of boiling point against log relative retention time where n-pentane was used as a standard with assigned time of unity. His data are transferrable to other columns of the same solvents provided n-pentane is first run on the other column at or near the same temperature.

Tenney concludes that the dipropionitriles such as β,β'-oxydipropionitrile are the most generally useful

solvents for type selectivity. As a neutral or boiling point column, Tenney recommended polypropylene glycol of molecular weight 2000 for oxygenates. For hydrocarbons he chose squalane. (The data of Eggertsen et al. in Table 8-1 suggest SF-96). He found that ethers were relatively easily separated from other oxygenates except acetals (80 to 90°C boiling point spread mixtures being completely separable). Alcohols could be separated from other types over a boiling point range of 15°C on a silicone column. Ketones and aldehydes could not be separated on a type basis. A technique for doing this will be presented later.

Data from other sources show that, compared to other types, alcohols are retarded on polyol solvents and emerge early on nonpolar solvents.

Compounds containing carbon, hydrogen and oxygen are the subjects of almost all the papers on GLC, with hydrocarbons claiming the lion's share. A complete bibliography would show scattered papers on sulfur compounds in petroleum, alkyl halides and so forth. Many of these are touched on elsewhere in this book. Usually these separations are by boiling point and offer no new principles.

CHEMICALLY ACTIVE COLUMNS

One paper will be mentioned here because it describes work with the very reactive boron hydrides (437). Extreme precautions had to be taken to keep oxygen and moisture away from the column during the analysis. The solvents consisted of paraffin oil, Octoil S and tricresyl phosphate, impregnated on Celite.

At the opposite pole from the above are the chemically active stationary phases for GLC. Here separation is achieved by complex formation or by chemical reaction. Silver nitrate dissolved in a polar solvent retarded Type I olefins (CH_2=CHR) in the work of Tenney.

Kerr and Trotman-Dickinson (602) used a mull of sodium bisulfite in ethylene glycol to react with aldehydes, but not ketones. The aldehydes could then be determined by comparison with a similar separation without the bisulfite. For removing olefins, these workers used a formula of 9 parts of mercuric acetate, 3 of mercuric nitrate and 20 of ethylene glycol per 100 of support.

Phillips (478) employed low melting metal salts as solvents to achieve some interesting separations. He reported that -picoline and 2,6-lutidine require 250,000 plates of silicone (1/4 mile) for separation equivalent to one centimeter (4 plates) of zinc stearate.

MIXED SOLVENTS

Columns containing mixed solvents are often a short-cut to finding a single solvent with the desired properties. If two solvents separate a sample in two different ways and something in between is needed, they may be mixed. If they are unreactive they may be blended before impregnation. This has the advantage that each particle of support has both solvents coated on it and any leading or tailing reducing property of either solvent is available throughout the column. In terms of retention times, the same effect may be achieved by using each solvent in its own column, and connecting the columns. This also has an advantage, that one can be shortened if the proportions are not right.

The most complicated mixed column recalled by the writer was used by Davis and Schreiber as the partition column in their gas analysis work reported in Chapter 5, and attributed by them to Block and Hochgesang. It consisted of 30 ft. of 30% solution of 23% ethyl benzoate and 77% dimethylformamide, followed by six feet of 25% dimethylsulfolane. The first section contained the volatile solvents which were retained by the dimethylsulfolane, so that they did not contaminate the Molecular Sieve 5A column to be used for the gas analysis portion of the separation. The early section was reimpregnated in situ as needed.

Other mixed columns have included a short section of Molecular Sieves to retain normal paraffins, as described earlier. As they are adsorbents and would cause tailing, Whitham used squalane as a tailing reducer for kerosine work. For gas oils the squalane was too volatile, but he found that by operating the sieve portion at 320°C tailing was greatly reduced.

Knight (604) used a blend of nonpolar diisodecylphthalate and polar triethylene glycol solvents for the work with allyl amines described in connection with tailing. The combination produced a series of evenly spaced peaks, while

neither solvent alone was useful.

HIGH TEMPERATURE COLUMNS

In high temperature GLC the stationary phase problems that are avoidable or sufferable at low temperature are often magnified. There are more isomers to contend with, they have smaller differences in vapor pressure and in solvent-solute relationships, and the solvents available to cope with them are more restricted. Even the analysis of low boiling samples suffers if the temperature is raised. The vapor pressure ratio of ethyl alcohol to ethyl ether is 10 at 20°C, only 3 at 100°C. At the same time the activity coefficients tend to approach each other at high temperature. Thus temperature has a definite effect on selectivity. Finally, there is the problem of keeping the solute molecule itself in one piece as it passes through the apparatus.

All of these problems are alleviated by working at the lowest practicable temperature. Short columns are indicated, with fine support for maximum efficiency and low solvent concentrations. In this way a wider variety of solvents can be used. Low sample sizes are necessary, as with large samples flat-topped peaks may result. The height of the peak is limited by the vapor pressure of the material.

The effect of operating pressure has been debated in the literature. Some early workers thought that if reduced pressures were employed the temperature could also be reduced. Actually this is true only if the pressure is below the vapor pressure of the sample, and at this point there is little carrier left. The present view is that reduced pressure increases detector response by increasing the concentration of sample, but that it also increases velocity gradient, reducing efficiency. Some workers feel that the overall result is beneficial.

Felton (385) and Dal Nogare and Safranski (625) have reported successful work at temperatures up to 300-350°C. They used Dow Corning high vacuum silicone grease, stabilized by pretreatment at 400°C.

Adlard and Whitham (526) reported a variety of high temperature separations. Their curves for methyl esters, to C_{34}, benzyldiphenyl separation into its isomers,

and waxes to C_{40} are shown in Fig. 8-6.

COLUMNS FOR TRACE ANALYSIS

In trace analysis minimum columns are also helpful, for peak width increases with retention time and low, broad peaks are less readily distinguishable from baseline noise than early, high ones. Some baseline noise is inevitable where equipment is being pushed to its limit for trace analysis work. In the same way, it is important to select a solvent in which the trace material has a high activity coefficient, so that it will emerge early. Small peaks are particularly difficult to measure if they are on the tail of a large preceding peak, so the activity coefficient of the major components should be low.

Where a suitable solvent is not available, it is possible to trap the impurities away from the bulk of the sample and analyze the trap contents with greatly reduced interference (368).

Bennett et al. (535) have reported a number of trace analyses. They used a DC amplifier to increase the signal from a thermistor thermal conductivity bridge. Their effective recorder sensitivity was 100 microvolts or less. Fig. 8-7 shows their analysis of benzene containing 70 ppm of isopropyl alcohol. Note that the major peaks were off scale. If insufficient attenuation is available, two runs can be made with different sample sizes and peaks common to both can be used to tie them together, or a marker can be added.

Combined high temperature and trace analysis presents a special problem in that small samples are not possible if traces are to be detected. This aggravates the high temperature problems since the temperature must be high enough to avoid flat peaks. Here might be an important use for some of the new sensitive detectors - for trace analysis at lower temperatures than otherwise possible.

There is a special kind of trace analysis in which traces of relatively high boiling materials are determined in fixed gases, in particular, in air. The fixed gases separate so readily from the trace materials that no special stationary phase problems are involved.

Chapter 9

COLUMN CONSTRUCTION

H. S. Knight

Shell Development Company

AFTER A PACKING is available, the next problem is what kind of material to put it in. Some common materials include copper, aluminum, stainless steel and glass. The former two have the advantage of convenience, the latter are less reactive and possibly less catalytic. For all around utility stainless steel is probably preferable. Most commercial equipment has stainless detector assemblies and columns. Glass is sometimes used for high temperature work, or where U-shaped columns that can easily be repacked are employed. Ellis and Iveson (569) used monel or nickel columns for halogens.

COLUMN GEOMETRY

The column should be as long as necessary to accomplish the desired separation, and no longer if time is a factor. With modern plate efficiencies on the order of 1000 plates per ft. most problems can be solved with columns less than 10 ft. long. For that "lone stubborn pair" consider a combined GLC-spectroscopic or two-column analysis rather than a long column with attendant problems. However, long columns do have increased sample capacity, in proportion to the square root of the length (439) and larger cuts can be taken. For gas analysis long columns will continue to be desirable.

There is no comprehensive study of column diameter that takes high efficiency columns into consideration. Probably 3/8 in. standard tubing is little worse than 1/4 in. with larger sizes falling off in efficiency. However, Evans et al. (570) report that columns up to 75 mm in diameter show no loss in efficiency under their conditions. They packed their 16 ft. columns with Celite impregnated with the solvent, and employed special vaporization chambers and detectors designed for high gas flow for the larger sizes. With mass spectroscopy and micro-infrared techniques, large columns are seldom needed for purely analytical purposes.

Straight and U-shaped columns are less likely than coils to permit channeling as the packing settles, and can be easily repacked if desired. However the writer is unaware of any evidence that coiled columns are less efficient, and coils will continue to be used for convenience and compactness.

PACKING THE COLUMN

The following technique for preparing columns is probably used by the great majority of gas chromatographers with but minor variations.

The support is weighed into an evaporating dish. The nonvolatile solvent is weighed in a suitable vessel and dissolved in enough volatile solvent to wet the support. If two nonvolatile solvents are to be used it is often preferable to blend them at this point. The solution is added to the support and the mixture stirred on a steam bath (a hot plate is slower) until the packing looks dry. Fine packings particularly tend to spatter during this operation. Continue the drying with occasional stirring until the odor of the volatile solvent is gone. Do not use a vacuum oven unless the high boiling solvent is certain to be nonvolatile under the oven conditions.

Place a plug of glass wool in one end of the tubing and pour the packing in the other end through a funnel, vibrating the column with a massage vibrator, or eccentric, or tapping it vigorously on the floor the while. If the column is long it may be bent into a U and packed from each end. When it is full to within one cm from the top, pack the re-

maining space about half full of glass wool.

During these operations record the weights of the materials used, so that the data may be reported in a suitable manner.

N.B. Do not pack the column with dry support and impregnate it in situ unless experience has shown that an efficient column will result. One 20 ft. column so impregnated had only 1000 plates.

Chapter 10

SAMPLE INTRODUCTION

S. A. Greene and E. F. C. Cain

Rocketdyne Research

IN GAS CHROMATOGRAPHY, sample introduction and sample size are extremely important because of their influence upon the apparent retention volume, the shape of the peaks obtained, and subsequently upon the ability of a given column to separate the components of the sample. Several authors (5, 117, 316) have discussed the theory of gas chromatography and utilizing the plate theory of Martin and Synge (5), and Porter, Deal and Stross (292) have studied the problem of sample introduction and sample size in gas liquid partition chromatography. The plate theory of Martin and Synge involves several simplifying assumptions which are as follows:

1. Samples are charged to the head of the column so that the initial charge is instantaneously contained within the first theoretical plate.
2. The partition coefficient for the distributing material is constant throughout the column.
3. No change in the volume of a volume element of mobile phase occurs as it passes through the columns.
4. All rate effects can be taken into account by the concept of theoretical plates.

The first two assumptions are important when considering sample introduction. By utilizing equations which describe the concentration of the solute as a function of the volume of the eluting gas, two extreme cases were considered. The first case has been designated "plug" flow and corresponds to a plug of solute gas mixture of constant composition being charged to the head of the column. The other case corresponds to mixing of the mobile phase in a vaporizer in such a manner as to introduce the vapor without dilution to the head of the column initially, but the sample concentration falls off exponentially with time to zero. Mathematically, plug flow gives rise to symmetrical peaks while exponential flow gives rise to peaks having a definite tail. In practice, the normal method of sample introduction will be somewhere between the two cases which have been considered.

Porter et al. (292) compared elution curves, which were calculated on the basis of "plug" flow and exponential flow, with an elution curve obtained by means of their instrument which had a sample introduction system

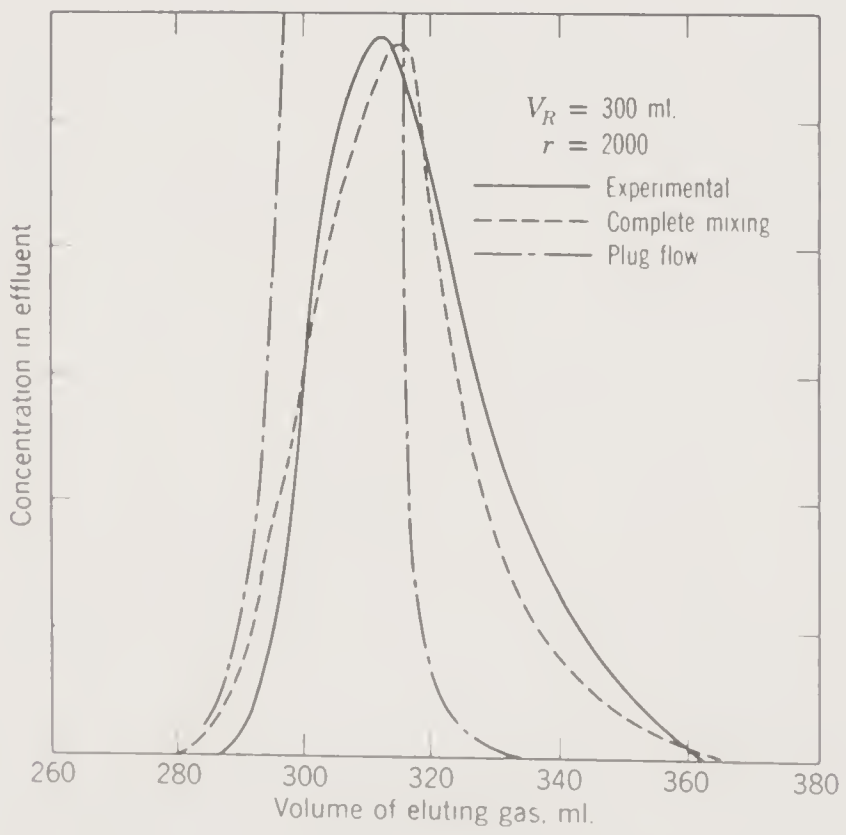


Fig. 10-1. Comparison of experimental and theoretical elution curves, assuming a retention volume of 300 ml and 2000 theoretical plates. Courtesy of Journal of the American Chemical Society (292).

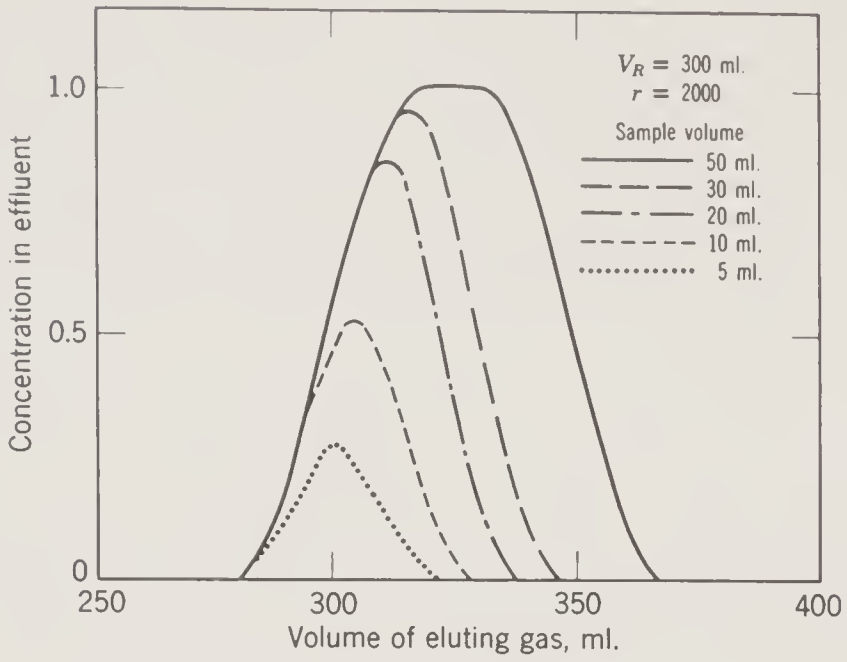


Fig. 10-2. Elution curves for variable sample of constant concentration. Courtesy of Journal of the American Chemical Society (292).

containing a heated vaporizer block at a distance from the column head. The sample was introduced into the heated vaporizer block, vaporized at some indeterminate rate and carried to the column head by the mobile phase. The experimental conditions were chosen such that the activity coefficient was nearly unity and thus the partition coefficient was nearly constant throughout the column. The results of this comparison are shown in Fig. 10-1. It should be noted that the experimental curve closely approaches that calculated for exponential flow.

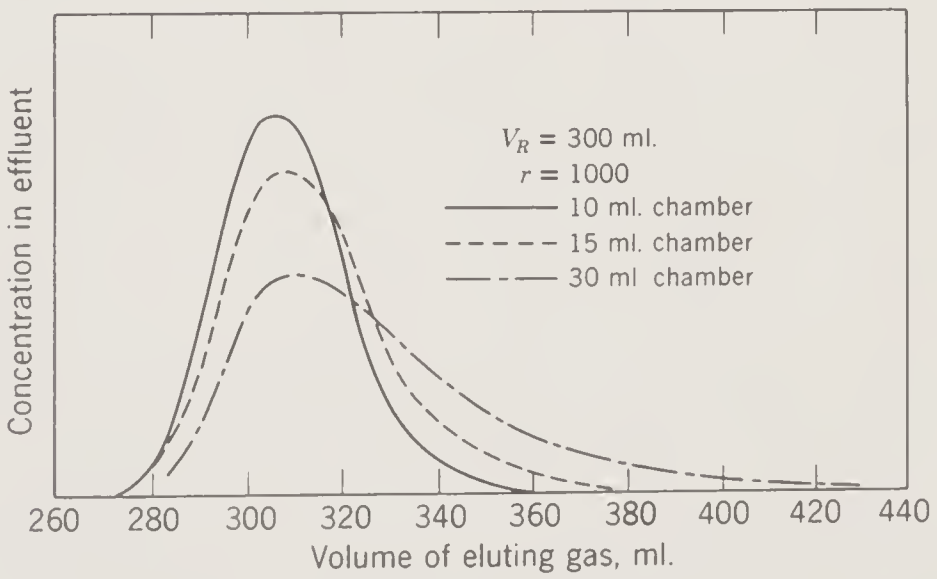


Fig. 10-3. Elution curves for constant sample size with variable charging time. Courtesy of Journal of the American Chemical Society (292).

Porter et al. calculated the effect of varying the sample size while holding the concentration of the sample in the mobile phase constant. This corresponds to varying the sample size under "plug" flow conditions and the results of this calculation are shown in Fig. 10-2. These authors have also considered the variation of charging time at constant sample size for exponential flow. The results of this calculation are shown in Fig. 10-3.

It is obvious from the above discussion that to obtain maximum column efficiency and accordingly narrow sharp peaks, the sample should be as small as possible and introduced in a high concentration as a "plug" flow.

The use of a small sample size should also be considered on the basis of the activity coefficient of the sample in the stationary phase. If a perfect solution is formed between the sample and the stationary phase, the resultant chromatographic peak is symmetrical if the other assumptions which have been stated previously are valid. However, as is often the case, the sample does not form a perfect solution with the stationary phase and tailing or leading can

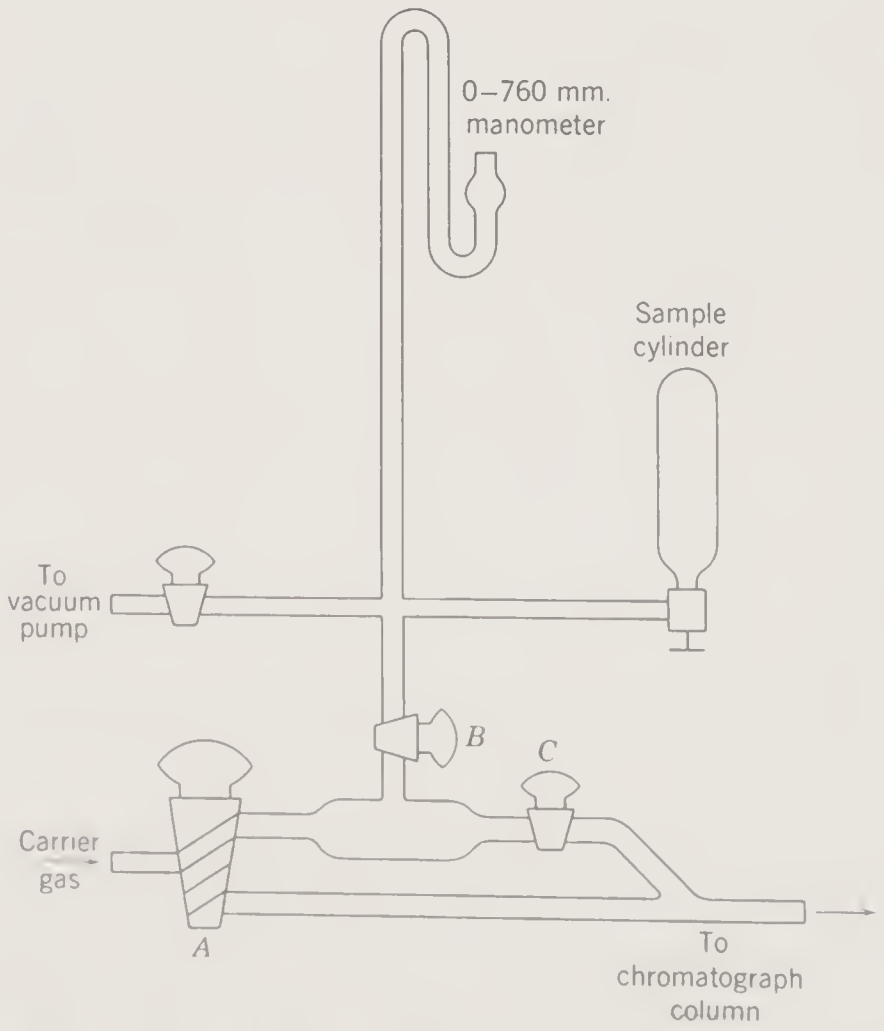


Fig. 10-4. By-pass system. Courtesy of Analytical Chemistry (475).

result, but if the sample is small, the resultant concentration of the sample in the stationary phase approaches extremely low concentrations and ideality. That is to say, if under a given set of chromatographic parameters, an unsymmetrical peak is obtained, the resultant peak can be made more symmetrical by reducing the sample size.

BY-PASS AND VALVE SYSTEMS

The introduction of gaseous samples into a gas chromatograph has generally been accomplished by means of either a "by-pass" system or a six port gas sample valve. Both of these systems are designed to introduce a known volume of gas sample into the mobile phase. The simple "by-pass" system used by Percival (475) is shown in Fig. 10-4. By calibrating the sample volume between stopcocks A, B, and C an accurately known quantity of sample can be introduced into the instrument in the following manner:

1. Place stopcock A in the reverse position to that shown in Fig. 10-4, and close stopcock C. The mobile phase now flows through the pass line.
2. Attach sample cylinder to the system, open stopcock B, and evacuate the system.
3. Disconnect vacuum and introduce the sample into the system to the desired pressure as read from the manometer.
4. Isolate the calibrated sample volume by closing stopcock B.
5. Introduce the sample into the column by simultaneously reversing the position of stopcock A to that shown in Fig. 10-4, and opening stopcock C.

Other authors (189, 575) have used similar systems which allow for interchangeable sample volumes and make the operation of only a single stopcock necessary to introduce the sample.

Most commerical instruments have employed a modification of the six port gas sampling valve. Fig. 10-5 shows a diagram of one modification of this type of valve which is available commercially. The gas sampling valve is generally connected to some type of gas handling system which allows the sample to be introduced into the valve with-

out contamination. The sample size is determined by the volume, the presure and the temperature. Referring to the diagram, the sample is introduced into the sample valve, when the valve is in position 1. When the desired sample is contained within the sample volume tubing, the valve is moved into position 2. At this point the mobile phase sweeps through the sample volume introducing the sample into the chromatograph in a condition which approaches "plug flow". The major advantage of this system over the by-pass system is that while it can be connected to a gas handling system and used in the same manner as the by-pass system, it can also be used in a gas stream, where repetitive sampling is desired.

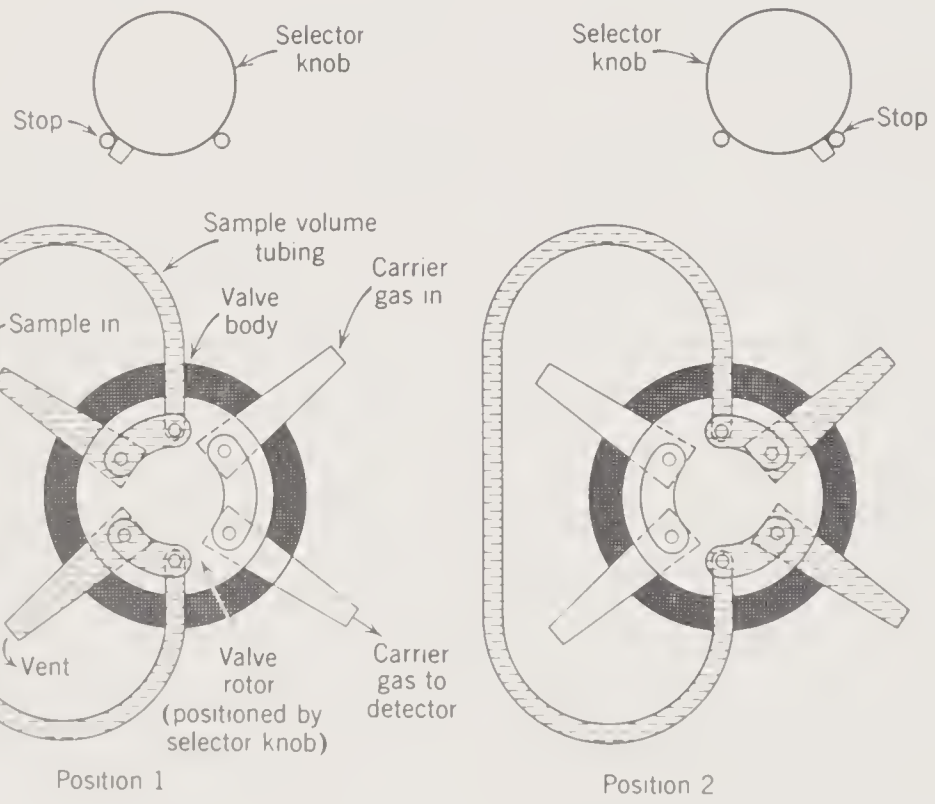


Fig. 10-5. Precision gas sampling system. Courtesy of Perkin-Elmer Corporation.

Tenney and Harris (507) have developed a gas pipet method of sample introduction. However, since this method has been used more commonly in liquid sample introduction, it will be discussed in detail later. Smith, Swinehart, and Lesnini (642) have described a system in which standard vacuum stopcocks, (hollow, precision-ground, 2 mm, oblique bore) have been used as a gas sample introduction system. Lubricated syringes have also

been used to inject a gaseous sample into a chromatograph, but this method is relatively crude and is recommended only for qualitative analysis.

LIQUID SAMPLES

The satisfactory introduction of liquid samples has in general been more difficult because of the limitation upon sample size. The most common way of introducing a liquid sample has been by means of a syringe and hypodermic needle. The sample is injected through a self sealing serum cap into the head of the column or into a vaporization chamber from which the sample is rapidly vaporized and carried by the mobile phase to the head of the column. The major problem encountered with this method of sample introduction is the difficulty of the mechanical introduction of an extremely small liquid sample into a relatively high pressure gas stream. The use of 1/4 ml syringes has been common but not very satisfactory since the generally desired liquid sample size is approximately 10 microliters. Recently, micro syringes having 10 microliters capacity, as well as smaller sizes, have become commercially available, and have proven to be very satisfactory in most cases. (See Appendix I B).

As mentioned previously, the liquid sample is generally introduced through a serum cap to the head of the column or into a flash vaporizer. If a small liquid sample is injected into the head of the column in such a manner that the tip of the hypodermic needle is level with the top of the column packing and the sample is injected very rapidly, ideal and desired conditions are approached very closely. However, if the sample is introduced into the space above the column packing, the sample introduction conditions will be somewhat less ideal and the separation will tend to be impaired. A simple diagram of this type of sample introduction system is shown in Fig. 10-6.

If, however, a flash vaporizer system is used, the sample is introduced by means of the syringe through a serum cap into a heated vaporizer block through which the mobile phase is flowing. The vaporizer is maintained at a temperature sufficient to insure rapid vaporization of the sample. During this period, the mobile phase is trans-

porting the vaporized sample to the column head. The result of this system is that the sample is introduced to the column at some indeterminate rate. However, since the sample size is generally very small, the influence of rate is minimized and the system is satisfactory.

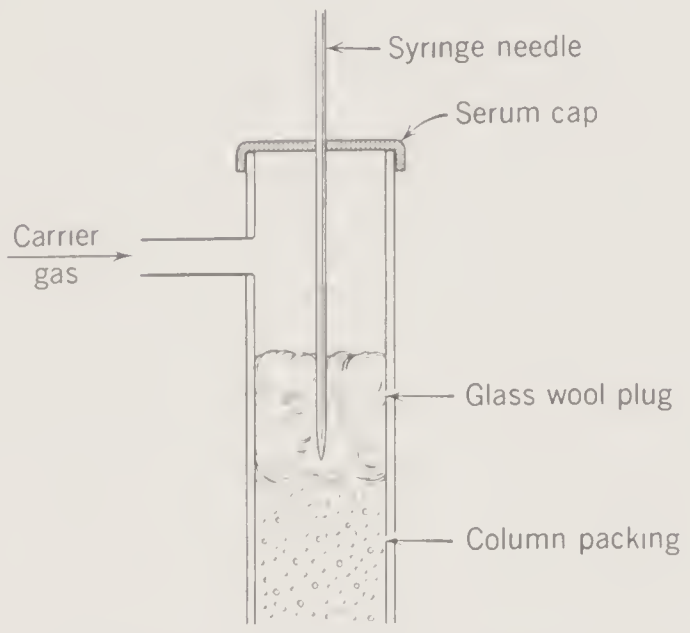


Fig. 10-6. Sample introduction to column head.

The main difficulties which have been encountered with syringe sample introduction are the small sample size, reproducibility, and problems associated with time lags which change retention times. The advent of commercially available micro syringes has allowed a much closer control of sample size than was possible with the standard 0.25 ml

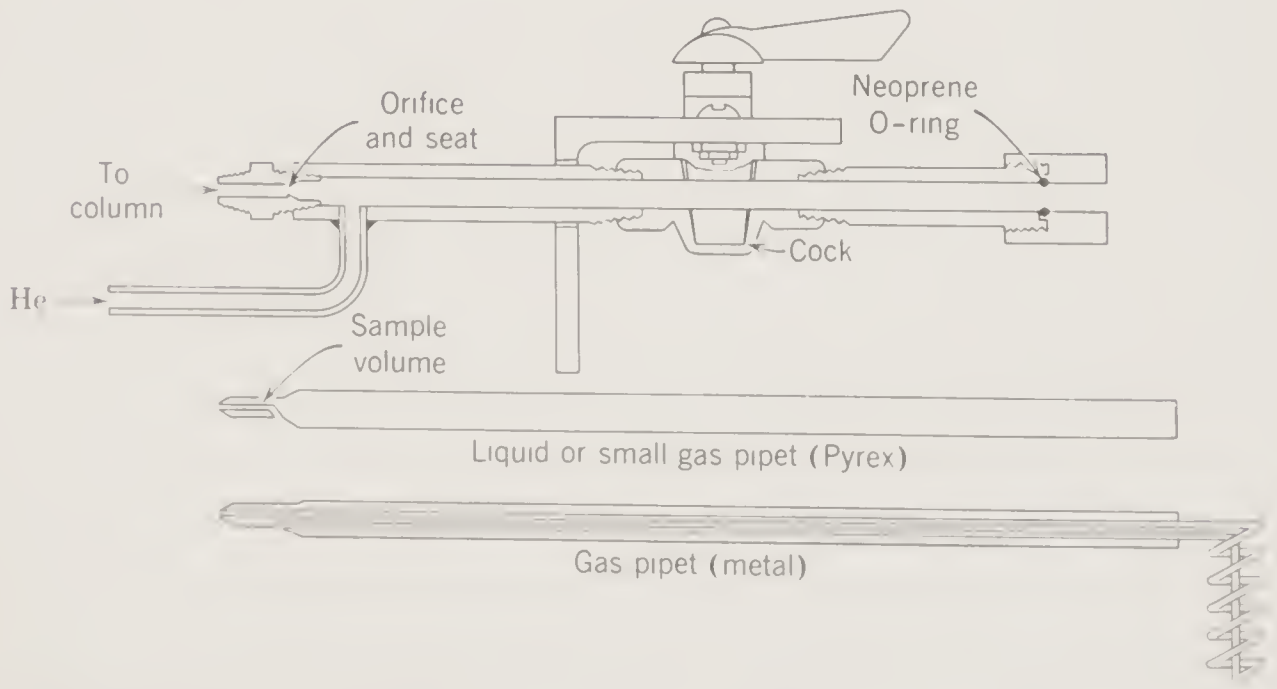


Fig. 10-7. Micro-dipper system. Courtesy of Analytical Chemistry (507).

syringe. The problem of introducing a reproducible sample volume has not been completely solved with the micro syringes, but a precision syringe, which has a reported accuracy of 0.1% and interchangeable capacities of 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 ml is also available commercially.

Tenney and Harris (507) have developed a precision liquid sample introduction system which is shown in Fig. 10-7. The sample introduction system is attached to a heated vaporizer block and operates as follows: The large cock is cracked slightly allowing the mobile phase to flush air from the system to the outside past the "O" ring. After the special pipet is filled by means of capillary action, it is slowly inserted into the tube until the pipet handle forms a seal with the "O" ring. The large cock is completely opened and the sample in the pipet is now under the pressure of the mobile phase in the chromatographic system. The pipet is now inserted through the large cock until the tip is in contact with the orifice and seat, at which point a differential pressure across the pipet is developed and the sample is swept into the heated vaporizer block and subsequently to the column. The authors report a precision at the 95% confidence level of ± 0.89% using a pipet of 0.00159 ml capacity. In the same manner, gas samples can be introduced by means of a gas pipet which is also shown in Fig. 10-7.

A third method of precision sample introduction was reported by Dimbat et al. (198). The method depends upon the introduction of a weighed liquid sample which has been sealed into a glass ampoule. The prepared ampoule is introduced into a special "by-pass" sample introduction system which is equipped with a bellows crusher. The sample expansion chamber is isolated and can be evacuated. The ampoule is crushed and the sample vaporized into the expansion chamber and subsequently introduced in a manner similar to the introduction of a gaseous sample. However, the sample size must be controlled so that the final pressure in the sample volume does not exceed the saturation pressure of the sample at the operating temperature. While this method is cumbersome, the introduction of a weighed quantity of a liquid sample is possible.

The sample introduction systems, which have been discussed, have proved satisfactory for many applica-

tions. However, as the use of the gas chromatograph has increased, special sampling and sample introduction techniques have been reported. It is impossible to review all of them in this short discussion, but a survey of several new techniques will serve as a guide to possible variations on standard methods or to the development of new techniques.

SPECIAL TECHNIQUES

In the field of organic chemistry, gas chromatography has been used to separate materials of high molecular weight and to determine the n-paraffin distribution in waxes. Ogilvie et al. (629) introduced the sample by injection from a hypodermic syringe through a rubber serum cap. The samples for which high temperature gas liquid chromatography is used are usually either solids or viscous liquids. To introduce this type of sample, the sample and the syringe were heated by an infrared lamp until the sample was fluid enough to be drawn through the needle. The sample introduction was made immediately while the sample was still liquid. An alternate procedure was to dissolve the sample in a lower molecular weight solvent which would have a relatively short retention time and would not interfere with the desired analysis. Care must be taken to use a hypodermic needle long enough to introduce the sample onto the hot portion of the column. Dal Nogare and Safranski (625) used similar methods of sample introduction in their work with high temperature gas liquid chromatography. Quin and Hobbs (635) also employed the solution technique of sample introduction by introducing a methanol solution containing a few milligrams per milliliter of the esters of nonvolatile acids directly into the chromatograph.

Because of sensitivity of the gas chromatographic technique, it has been applied to the field of trace analysis. Eggertsen and Nelson (568) determined the C_2 to C_5 hydrocarbons from engine exhausts and the atmosphere. The sample sizes used ranged from a few hundred milliliters of exhaust gas to 5 to 10 liters of air. The samples were passed through a trapping column at liquid oxygen temperatures to concentrate the samples. After the sample was collected in the trapping column, it was connected to the separating column while still cold and purged with helium for 20 to 30

min. This removed most of the material boiling below the C_2 fraction. After flushing, the trapping column was quickly warmed and the sample was eluted through an Ascarite column to remove water and carbon dioxide from the sample and then through the separating column. This system emphasizes two techniques which have been employed in gas chromatography sampling. The first is the use of a trapping column to concentrate the sample and the second is the use of an auxiliary precolumn to remove interfering substances.

West et al. (656) have proposed the use of cold activated charcoal columns to collect trace quantities of organic air pollutants. The cold collecting columns are transferred to the chromatograph and the sample introduced directly from the collecting column to the analyzing column. The method was applied satisfactorily in the range of 1 to 50 ppm of organic air pollutants with an efficiency of approximately 80%.

Boggus and Adams (539) employed a gas liquid chromatograph as the concentrating system in the analysis of chloroethane. A 1 ml liquid sample was introduced into the concentration chromatograph by means of a gas sampling valve. The separation was carried out and the trace contaminants collected in a U-tube which was immersed in liquid nitrogen. The U-tube was then fitted onto the second chromatograph, warmed, and the contaminants were analyzed directly. It was reported that materials in concentrations as low as 1 ppm could be determined.

Simmons and Snyder (641), however, employed two or more gas chromatographic columns in series such that the preliminary cuts obtained from the first chromatograph could be charged directly into another chromatograph. This arrangement of instrumentation allows the detailed analysis of a complex mixture without having to prepare separate samples.

From the above discussion, it is apparent that sample introduction and sample size are parameters of gas chromatography which can be varied to meet the desired conditions of the analysis and that judicious choice of the techniques which are employed can have a large effect upon the results of the analysis or separation which is being carried out.

Chapter 11

TEMPERATURE CONTROL

C. M. Drew

U.S. Naval Ordnance Test Station

THE TRANSPORT VELOCITY of a sample component through a column is directly dependent upon the distribution of the component between the stationary and moving phases. Separations are only possible where there is a different distribution between the compounds under consideration. The distribution is also a strong function of temperature and the column must be operated somewhere between the two limits of distribution, i.e., where the compounds are completely adsorbed in the stationary phase or completely desorbed. Obviously no separations could be achieved under conditions of either of these extremes. Increasing column temperature will shift the distribution more in favor of the moving phase and thereby increase the transport velocity of all the sample components. In order to utilize the maximum effectiveness of the stationary phase it is necessary to choose a temperature low enough that the sample constituents are mostly distributed in favor of the substrate. Under these conditions the transport velocities will be small and the analysis will take a long time. Also, the peaks will be broad with resultant losses in sensitivity (peak height). In practice a compromise in temperature is selected to give reasonable analysis times without undue sacrifice in column resolution.

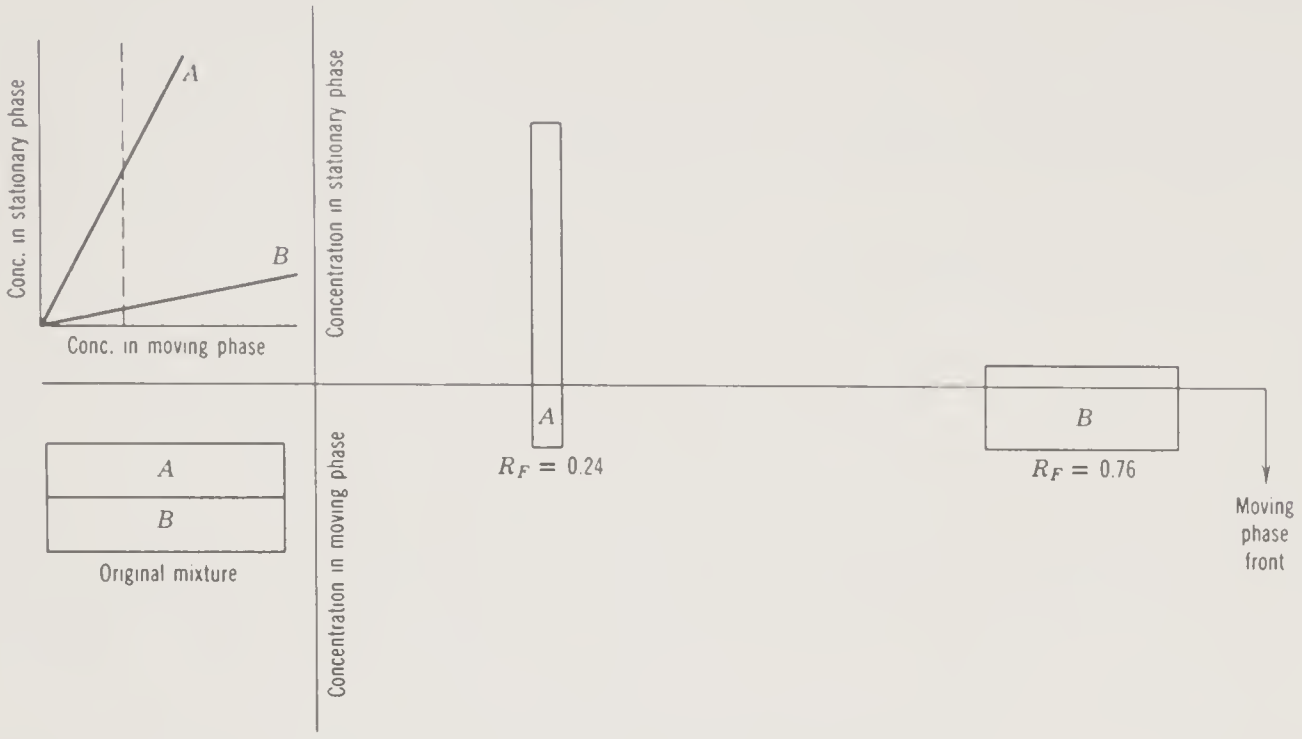


Fig. 11-1. Ideal linear chromatography. Courtesy of Reinhold Publishing Corporation (439).

GENERAL CONSIDERATIONS

Fig. 11-1 is a graphical representation of the separation of two compounds assuming ideal linear chromatography (439). This model involves only the essential features of chromatography. The band shape during its passage through the column does not change. Compounds A and B introduced originally at the head of the column as a mixture behave independently of each other and are separated only on the basis of their different partition coefficients. For a more thorough treatment of this subject, the reader is referred to Keulemans (439) and Wilson (4).

Effect of Temperature on Resolution. The effect of three different column temperatures upon a group of seven hypothetical compounds chosen for a wide boiling point range is depicted in Fig. 11-2. The resultant chromatograms so obtained are given for each example, but non-ideal chromatography was assumed in the latter instance so that the chromatograms would appear in their more conventional form. This model demonstrates the effect of column temperature where a wide range of boiling points are encountered, and further shows that no one temperature can be chosen to give a complete analysis. This is a typical problem en-

countered with many sample mixtures. In many cases it is not necessary or even desirable to analyze all the constituents so a temperature is chosen that will achieve the separations desired within a reasonable time.

Where it is necessary to have a complete analysis with an excessively large boiling range it is necessary to analyze duplicate or multiple samples at different temperatures or use tandem columns selected to complement each other. For example, the Perkin-Elmer Vapor Fractometer, Model 188, utilizes as many as three columns simultaneously. Another technique described later is continuous heating of the column during the analysis, a feature which is available on the Burrell Corporation Kromotog models.

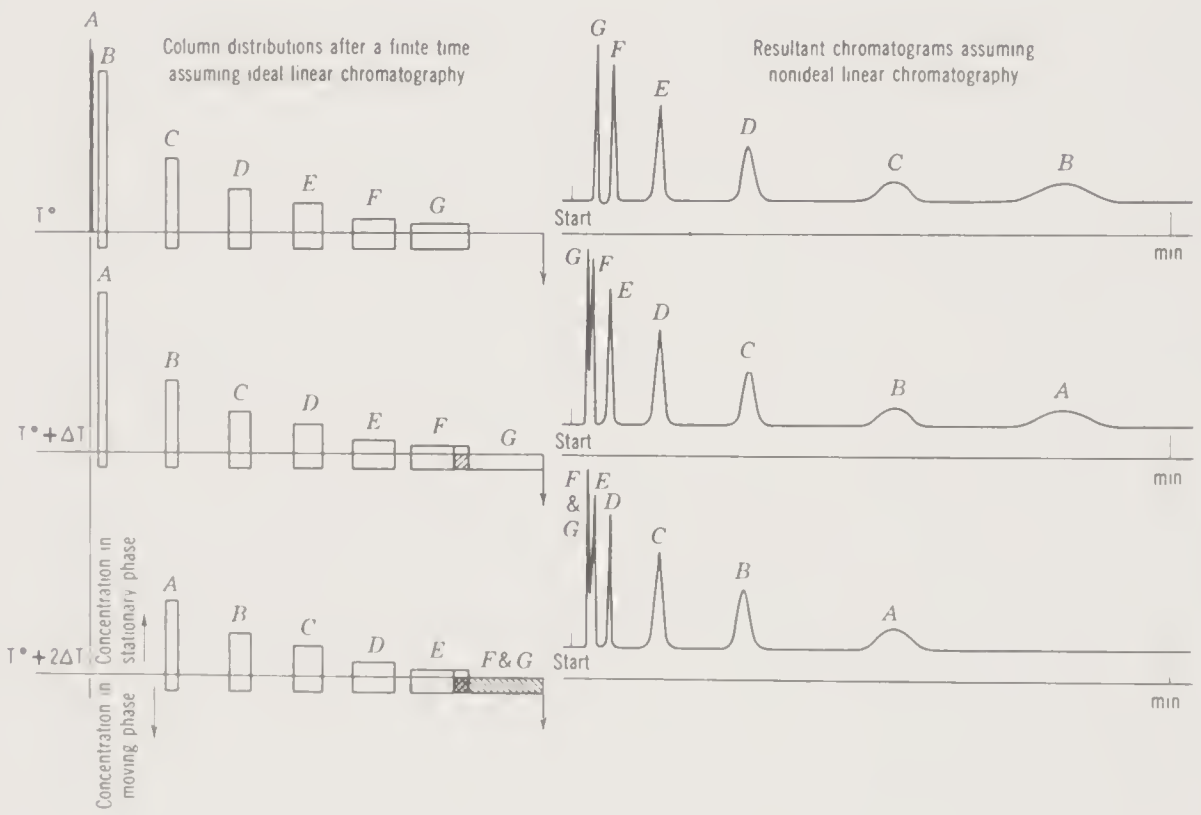


Fig. 11-2. Effect of column temperature on the resolution of a wide range sample.

Martin (271) recognized the potential of gas chromatography as a tool for the measurement of solution parameters such as partition coefficients, activity coefficients, effective vapor pressures, or Henry coefficients and heats of solution or vaporization. This is a different application for gas chromatography but it does provide basic information which is valuable for extending the analytical application of the method. Porter et al. (292) point out that the

heat of vaporization of the solute predominates in determining the change in partition coefficient with temperature, and that reasonable estimates of partition coefficients as functions of temperature can be based upon a single-temperature point. This would, in principle, allow the worker to predict an optimum column temperature or to determine, in the case of continuous heating, the temperature range over which the column should be operated.

COLUMN STABILITY AT HIGH TEMPERATURE

Relatively brief attention has been given to the longevity of column packings in the literature. It is quite apparent that the vapor pressure of the liquid substrate must be low enough at maximum column temperature to prevent volatilization of appreciable amounts of the liquid. Furthermore, the liquid should be thermally stable for reasonable periods of time, since any chemical change will have serious effects on its resolving behavior. Another important consideration is the possibility of reactions between the liquid substrate and the compounds being analyzed. Occasionally such interactions are utilized to facilitate resolution or detection but general practices rely primarily on physical factors to effect the separation. In general, chemical reactions which alter the character of the partitioning liquid should be avoided. Weak complex formation (solvation effects) on the contrary, are often very useful and their chemical reversibility insures no permanent damage to the stationary phase will result. Such an effect was used by Bradford et al. (110) specifically to retard terminal olefins by weak adduct formation with silver nitrate. In this case an upper temperature limit of about 40°C was imposed by the effect of temperature on the stability of the complex.

Migration of Substrate. One of the most serious problems encountered in high temperature chromatography is loss of stationary phase by migration of the liquid through the column packing (weeping). The problem is particularly pronounced with large diameter columns used in preparation work. The best solution is reduction in the amount of stationary phase. Simple calculations will show that adequate coverage of the surface area of the support

can be realized with only a few percent of liquid by weight. This does introduce some loss in column capacity since the volume of liquid substrate must be considered as well as surface area, but it must be remembered that under operating conditions the surface molecules of the liquid are those mostly involved in the process. These effects are treated in Chapters 4 and 5. The only other purpose for adding larger amounts would be to supply a reservoir from which losses could be tolerated for some time before depletion of the liquid from available surface. Actually, this only aggravates the weeping problem, and the residual film after the bulk of the liquid has evaporated or migrated away is undoubtedly held with more tenacity. One suggestion made to the author (683) is to place a short section of dry support material at the column exit. This provides for a time extension on the column life since any liquid migration will first have to saturate the uncoated surfaces before reaching the column exit.

This approach was criticized by Van der Craats (365). He feels that the loss of stationary phase is by evaporation and that there is no reason for condensation again. This view is correct insofar as it applies to evaporation losses at the exit end of the column. However, the phenomena of liquid exuding from the exit bears testimony to actual migration of liquid. Obviously a dry section will delay such a liquid front for a time. Furthermore, the mechanism for migration of the liquid substrate undoubtedly involves an evaporation condensation cycle - exactly the same process accounting for transport of the sample constituents along the column packing. Any appreciable vapor pressure of the liquid substrate would subject it to transport by the moving phase just as any other material in the column.

Another plausible explanation for the transport of the stationary phase is the solution effect of the sample constituents at high concentrations such as encountered in preparative columns. The condensation or solution of large amounts of sample components produces bands in the column of increased wetness on the packing with resultant decreases in the viscosity of the stationary phase, hence an increase in its mobility. Friction between the more mobile liquid film and the moving gas phase is more effective in driving the fluid along the packing. Other properties related to mobility such as capillary attraction, liquid diffusion

effects, and gravity are also more effective.

In some of the earlier publications workers reported stationary phase concentrations as high as 40% of the liquid by weight of inert support. The average value at the present time is probably around 20%. For high column temperatures the amount of liquid is frequently lowered to 10% or less.

For conventional detectors the column temperature is limited to a value just below that which produces excessive base line shift due to the presence of stationary phase in the carrier stream. This limit is quite arbitrary depending upon the choice of operators, but usually a rate of carry over not exceeding 1 mg per min is typical. For more sensitive detectors the limit is held to around 1 mg per hour. These limits would be considered quite excessive by many workers.

When the column temperature is programmed steadily upward during analysis the upper limit is reached when the base line takes a definite upward swing. At this point heating is stopped.

COLUMN CONDITIONING

Techniques for preparing columns require a high temperature conditioning treatment as part of the procedure. This serves to drive off residual solvents and other volatile contaminants. It also helps distribute the stationary phase over the inert support, and in some instances drive some chemical changes to completion that would ordinarily effect column behavior at lower temperatures. The author's experience shows that a bake should be done at maximum temperature with the exit of the column open (not connected to the detector or exit line) for about one hour with a normal or moderately higher than usual carrier flow rate. After noticeable vapors have been driven off, the exit line is then connected to the detector and the adequacy of bake out is judged by the detector output, i.e., the output observed when pure carrier is in both arms of the detector. Some workers recommend conditioning up to 24 hours in order to obtain reproducible column behavior. The time required is, of course, a function of the nature of the stationary phase, and it might be safe to state that any column showing change

after 24 hours is probably unsuitable for use and would never settle down satisfactorily.

APPARATUS REQUIREMENTS

Since numerous methods have been employed for controlling column and detector temperature, only brief mention will be made here of some of the methods in common usage. The physical apparatus employed for this purpose is relatively unimportant so long as it provides for adequate control, convenient change of columns, and rapid change of operating temperature. In general, the temperature of a column should be controlled throughout its entire length to within 0.1°C. If peak height measurements are used for quantitative estimations the temperature control is highly critical. Retention volumes are similarly quite temperature dependent, and where these are used to measure solution parameters or to calibrate columns, very careful attention must be given to the quality of temperature control.

Long Columns. Glass columns were first employed in the earlier developments of the method, and since it is not feasible to bend glass tubing after packing, it was necessary to use reasonably long straight sections. Two or more of these sections were then joined after packing with suitable connections to afford longer column lengths. Since glass tubing is commercially available in about four ft. lengths, it was common to use them as received for chromatography columns. In order to provide temperature control the thermostated region was necessarily a long narrow enclosure. This geometry does not lend itself readily to critical temperature control because of difficulties in uniform heat input and temperature distribution over such large areas. Curiously enough, there still is some tendency among manufacturers of commercial equipment and designers of self-made equipment to use long narrow enclosures. This is partially justified by the convenience offered in the storage of large numbers of straight four ft. long columns, and the quick change feature offered by such instruments as the recently introduced Pye Chromatograph.

Temperature regulation of long thermostats has been achieved nicely, however, by more than one method. The first arrangement employed was to surround the column

in a jacket fed with vapor from a constant boiling liquid (61, 89, 128, 137). The apparatus operates under total reflux with provision to return the condensate directly to the boiler. With suitable lagging it offers a very precise means of providing uniform temperature. Disadvantages in this method lie in the excessive warmup times, inconvenience of changing temperature, restriction of operating temperatures to the availability of liquids having the desired boiling points, and the difficulty of finding liquids stable enough or with high enough boiling points to operate at the higher column temperatures. Also, large amounts of hot boiling liquids are hazardous.

Another method frequently used even in modern equipment is an air bath provided with rapid circulation (321, 334). This method is also used by the author with a coiled column and will be described later.

Coiled Columns. Another common arrangement is the use of block heaters with the column in close enough proximity to the block (a suitably shaped mass of high heat conducting metal) to assure adequate temperature distribution. This method has many variations. Two examples of commercial equipment using modifications of this scheme are the Consolidated Chromatograph, and the Pye Argon chromatograph.

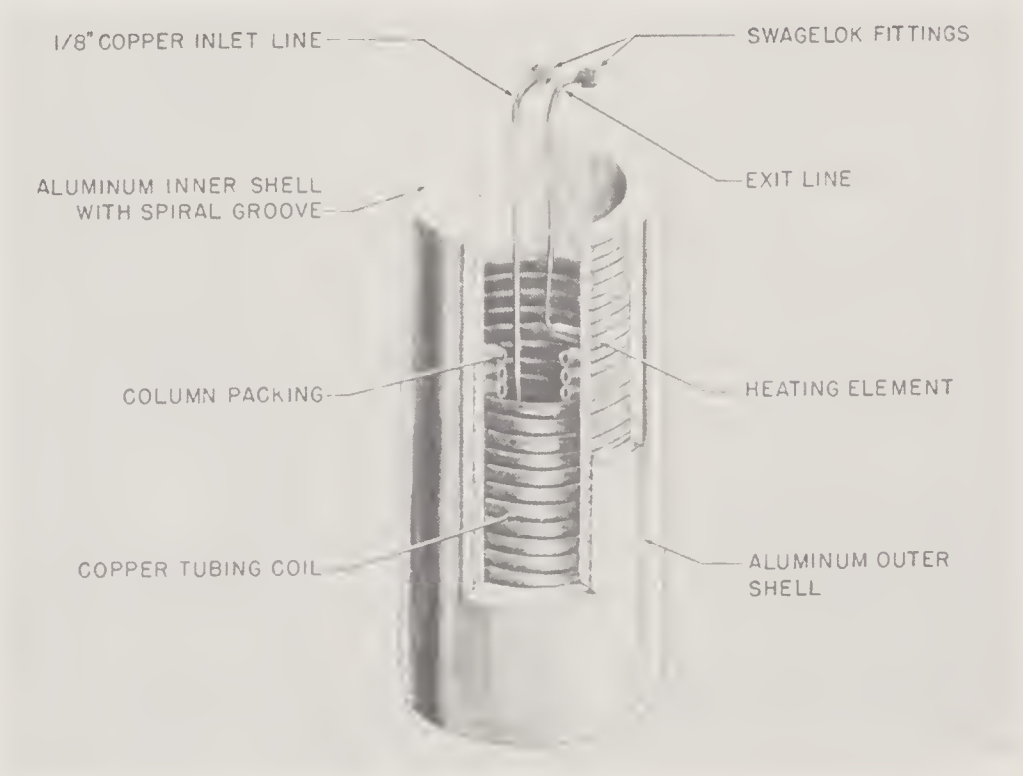


Fig. 11-3. Arrangement for programming column temperature. Courtesy of Butterworths Publications (203).

Fig. 11-3 is an example of an earlier model used by the author for continuous heating of the column. This apparatus is still in use by our laboratory; however, the circulated air bath arrangement mentioned above is a better method because the large mass of metal has been eliminated and this permits more rapid cooling or heating of the system and gives better temperature distribution. Columns have been thermostated by direct immerson in bath fluids or in refrigerants having suitable boiling or melting points. This method is entirely suitable but not in general usage.

One of the more direct approaches to the problem is the adaptation of a standard laboratory drying oven for the column and detector enclosure as in the Cenco Vapor Phase Analyzer.

A very compact and efficient unit specifically designed for high temperature work was devised by Felton (385). He made ingenious use of glow plugs as detector sensing elements incorporated within the same heating block used to control column temperature. Felton states, "In use the unit is wrapped with electrical heating tape or placed directly in a suitable oven."

TEMPERATURE CONTROL OF DETECTORS

Combined Control. The majority of analyses done by gas chromatography are at a fixed column temperature. For many detectors it is necessary to maintain them at a carefully controlled constant temperature. This is most conveniently done by including the detector assembly in the column thermostat. This has a further advantage of permitting very close coupling of the column exit line to the inlet arm of the detector. This arrangement can on occasion lead to objectionable condensation of high boiling fractions or liquid substrates within the detector cell block. A common practice is to supply a small additional heat input to the detector so that it will control at a few degrees higher than the column itself. This minimizes the condensation problem to a large extent.

Separate Control. An alternative scheme is separate thermostating of the detector from the column assembly. This method is highly recommended by the author since it

allows changing column temperatures without involving the temperature dependence of the detector. With this practice the detector is maintained at a higher temperature than the column.

There are some detectors whose output is not seriously affected by temperature changes. These include all the various ionization and hydrogen flame detectors discussed later. The main temperature requirement in this case is that of preventing condensation within the detector and adjacent lines between the column exit and detector inlet. A secondary requirement such as with rare gas (Argon) ionization system is the choice of a temperature compatible with optimum detector sensitivity to the sample constituents. It is interesting to note that with this detector improved sensitivity is observed at moderately high operating temperature, whereas with the more conventional thermal conductivity cells elevated temperatures generally produce losses in sensitivity. This is particularly true with thermistor type units. The seriousness of the effect can be judged from a recent Gow-Mac brochure accompanying their various detectors. Typical response curves are given in Fig. 11-4.

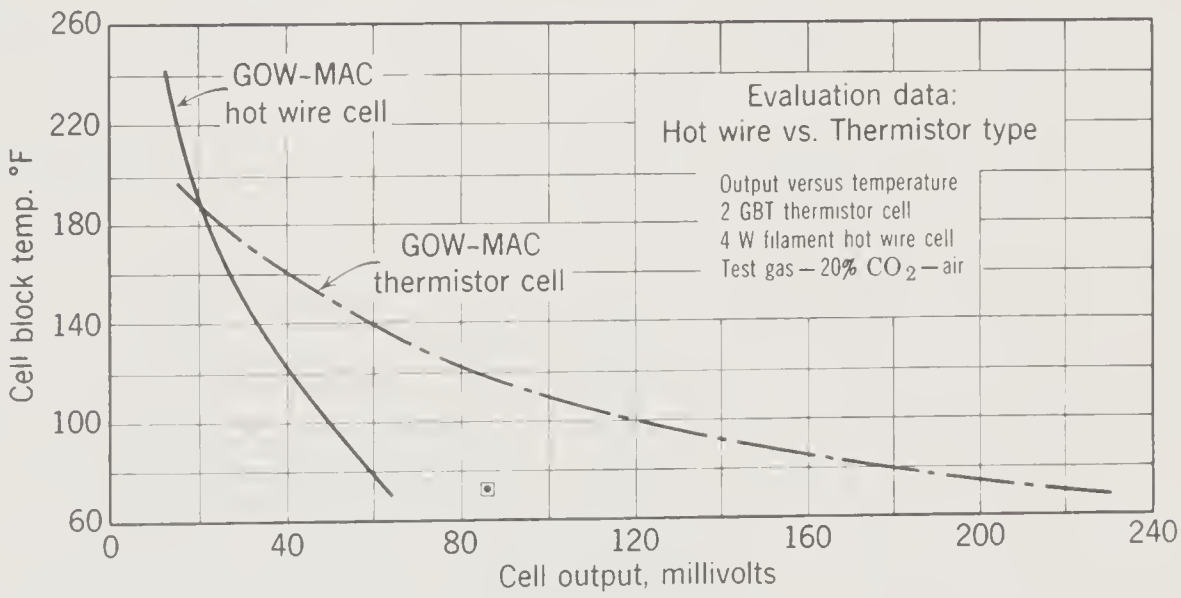


Fig. 11-4. Comparison of temperature on the output of thermistor vs. filament type detector. Courtesy of Gow-Mac Instrument Company.

VARIABLE COLUMN TEMPERATURE

Numerous articles have appeared in which continuous heating of the column is employed in order to obtain useful analysis over a wide span of boiling points (42, 203,

225, 491, 550, 587).

The author has employed this technique exclusively for a number of years in its application to the kinetic study of gas phase reactions (203). The convenient spread of elution peaks so obtained and the increased over-all resolution have been much superior for this type of sample mixture than results obtained with the constant temperature techniques. Continuous heating of the column can be more time consuming per sample than constant temperature chromatography because of the slow heating rate required in order to utilize effectively a reasonable column length and the necessity of returning the system to its original starting temperature for each analysis. The method has also proven generally unpopular because of several difficulties in maintaining zero base line drift. Most detectors employed in the United States measure thermal conductivity of the column effluent and they are quite temperature sensitive. Therefore, as mentioned earlier, they must be thermostated separately from the column. They are also somewhat flow sensitive but more important, if the pressure in the reference and measuring sides change relative to each other, the detector output changes. If the column temperature changes the viscosity of the carrier gas changes as an inverse function of column temperature, thus changing the pressure drop through the column. This effect is discussed by Clough (550). The resultant change in column flow is reflected as changes in back pressure in the measuring chamber of the detector, thus producing drift. Clough solved the problem by using a flow control device instead of a pressure regulator.

Although flow regulation ahead of the column is an effective means of overcoming these difficulties, the author uses a method which is equally effective and much simpler, and at the same time affords better column efficiency.

The problem of flow control is caused by dependence on the pressure drop through the column packing for establishing the flow rate. In practice an inlet pressure is chosen that will give the desired rate with the exit stream near or about atmospheric pressure. The variable flow problem has been solved by virtually eliminating the pressure drop through the column. An orifice is placed in the exit line and thermostated with the detector at constant temperature (Fig. 11-5). An inlet pressure considerably in

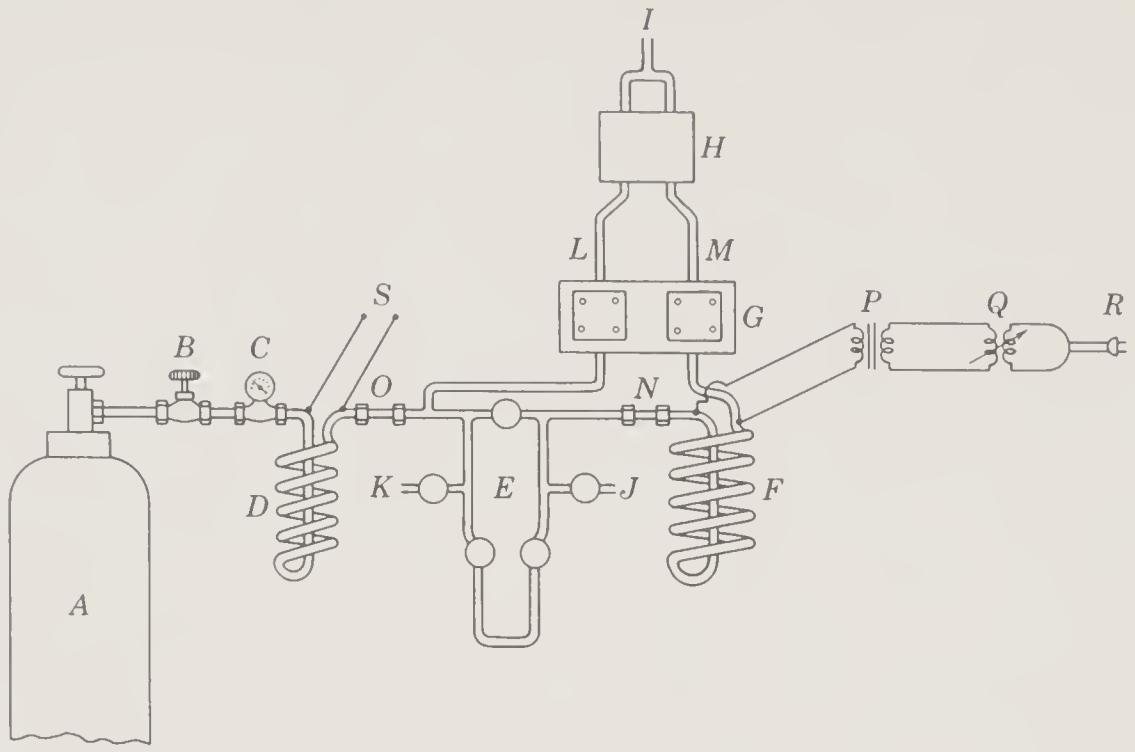


Fig. 11-5. Schematic arrangement for an apparatus permitting programmed heating of the column.

A. Helium Supply
B. Pressure Regulator
C. Pressure Gauge
D. Purifying Trap
E. Introduction System Valve Assembly
F. Column
G. Flow Control Blocks
H. Detector
I. Exit Line to Flow Meter and Traps
J., K. Vacuum Connections
L. Reference Stream
M. Column Effluent
N., O. Glass Inserts between Swagelok Fittings
P. 6-Volt 5-Amp Filament Transformer
Q. 5-10 Amp Variac
R. 110-V AC Power Supply
S. Switch to Provide Current to Bake out Purifying Trap

excess of that required to give adequate flow through the column is used. The orifice is restricted until the desired flow is obtained, hence the column is pressurized throughout its entire length and up to the orifice at essentially the inlet pressure. Actually, there is still some pressure drop through the column, but with a suitably high inlet pressure this is reduced to some negligible value. The exit line of the column is 1/8 in. thin wall stainless steel. The orifice is made by compressing this line between two metal blocks with tightening screws until the desired flow is achieved. There is enough resiliency in the metal tubing to allow for

some plus or minus variation; however, it is advantageous to leave the orifice at a fixed setting, thus assuring reproducible flows over extended periods of time. Measurements with a soap film flow meter have verified constancy of flow for well over a period of one year at a given inlet pressure. If another flow rate is desired, it is most easily achieved by changing the inlet pressure rather than adjusting the orifice. Wide variations require adjusting both or even installing a new line between the blocks and readjusting for the desired rate. The use of valves is not permissible because enlargements in the exit line produce sample dilution with carrier gas. This affects both resolution and sensitivity.

In addition to achieving base line control over extended temperature changes, column operation is improved due to the increased pressure of the carrier gas and the low pressure drop through the column. These effects have been treated in Chapter 4.

In Fig. 11-5 it will be noted that the exit lines from the measuring and reference arms of the detector block are connected to a common exit line after leaving the detector. A very slight restriction to flow is placed in this line to assure that both arms of the detector are at the same pressure, thus utilizing the fact that both arms of the thermal conductivity cell have nearly identical sensitivity coefficients of pressure. In the author's apparatus no appreciable base line drift is encountered over a column temperature range from -196° to $100^{\circ}C$, using a flow rate of 50 ml/min with 50 psi inlet pressure on a 14 ft. column packed with a 30-40 mesh particle size column material.

Since the importance of close column temperature control has been stressed in order to achieve maximum efficiency, it might appear that a closely controlled temperature program would be required for this technique. The difficulty of achieving this has no doubt discouraged many workers from using the method. It has been shown that the ratio of peak height to peak width is a strong function of column temperature. It is well known that peak areas, on the other hand, change very little with column temperature. Area measurements have proven to be more reliable for quantitative accuracy, hence close column temperature control is necessary only where utmost column efficiency is required.

OPTIMUM OPERATING CONDITIONS

With programmed heating, consideration must be given to optimum carrier flow rate and length of column as a function of heating rate. Ideally, at the start of an analysis all of the constituents of the sample mixture are condensed at the front end of the column. Incidentally, this insures a perfect start condition and eliminates the problems of band broadening brought about by failure to inject the sample properly. As the column warms, the most volatile material reaches a vapor pressure great enough to begin incipient migration through the column and it moves out ahead of the lesser volatile materials which presumably are still stationary. This is a thermal separation not realized to such a large extent at constant temperatures. Materials of nearly identical boiling point must depend upon the more recognized parameters affecting separations by gas chromatography. It is readily seen that as the temperature increases the transport velocity of any given material increases accordingly since the distribution of the solute is shifted into the moving phase and correspondingly less in the stationary phase. The upper limiting transport velocity is reached when all of the solute is in the moving phase. At this point the velocity of the solute is equal to the velocity of the carrier gas. If this happens before the solute reaches the end of the column the remaining length of column is not effective and only serves to broaden the band. Each successive fraction will experience about the same acceleration and reach its limiting velocity at about the same point in the column. The column should be just short enough to prevent this state being reached prior to emergence from the exit end. It is obvious, therefore, that there is a relation between optimum column length and heating rate, and that both these parameters are also dependent upon the flow rate of the carrier gas. These variables could conceivably be expressed mathematically in such a way as to allow the worker to predict his best operating conditions. At best this would be difficult even if the present status of chromatographic theory would permit such treatment. An empirical approach is relatively easy. Table 11-1 shows a set of operating conditions which are typical.

TABLE 11-1. OPTIMUM PARAMETERS FOR A 1/4 IN. x 14 FT. COLUMN

Column packing:	30-40 mesh, 1.5% Squalane or Pelletex
Column dimensions:	1/4 in. OD by approx. 3/16 in. ID by 12 ft. long
Column material:	Stainless steel tubing
Carrier gas:	Helium
Inlet pressure:	50 psi
Flow rate adjusted by exit restriction:	50 ml/min
Heating rate:	-196°C to 100°C/90 min (nonlinear)

With these conditions it was found that an 8 ft. column was less effective than a 12 ft. column, and no harmful effects could be observed with column lengths up to 15 ft.; however, this seemed to be the longest length that could be tolerated without noticeable loss in resolution due to excessive band broadening. The broadening effect was most serious with olefins which exhibit some tailing on this packing. A 30 ft. column operated under these conditions gave poor results with obvious spreading occurring in the unusable additional 15 ft.

COLUMN HEATING APPARATUS

The physical arrangement for cooling and heating the column can be achieved in a number of ways. One method mentioned previously in the text (Fig. 11-3), consists of an aluminum block provided with an embedded nichrome heater. The entire assembly is contained in a Dewar flask. Liquid nitrogen or other refrigerant is poured into the central opening until a suitably low temperature is achieved, after which it is removed and immediately the heater is turned on, controlled by a variable transformer set to give the desired heating rate. Since heat losses to the surroundings are minimized by the surrounding Dewar, the heat capacity of the system is the determining factor on the rate of heating versus voltage applied. Over reasonable ranges of temperature the rate of rise is reasonably linear. This system has worked satisfactorily for a number of years, but it is unduly time consuming since the large heat capacity of the

block requires a long time for cooling, and it also wastes considerable refrigerant in the cooling process. The purpose of the block is merely to provide a means of heating the column and distributing a uniform termperature along the column by means of the high heat conductivity of the aluminum metal. The latter was not achieved very satisfactorily because the lower end of the block was slow to heat, and temperature gradients of several degrees were obtained along the column, depending on its location within the block.

A different arrangement for this technique is shown in Fig. 11-5 and in the photograph, Fig. 11-6. The column is a 14 ft. length of coiled stainless steel pipe 304 1/4 in. OD by 3/16 in. ID. It is suspended in an air bath

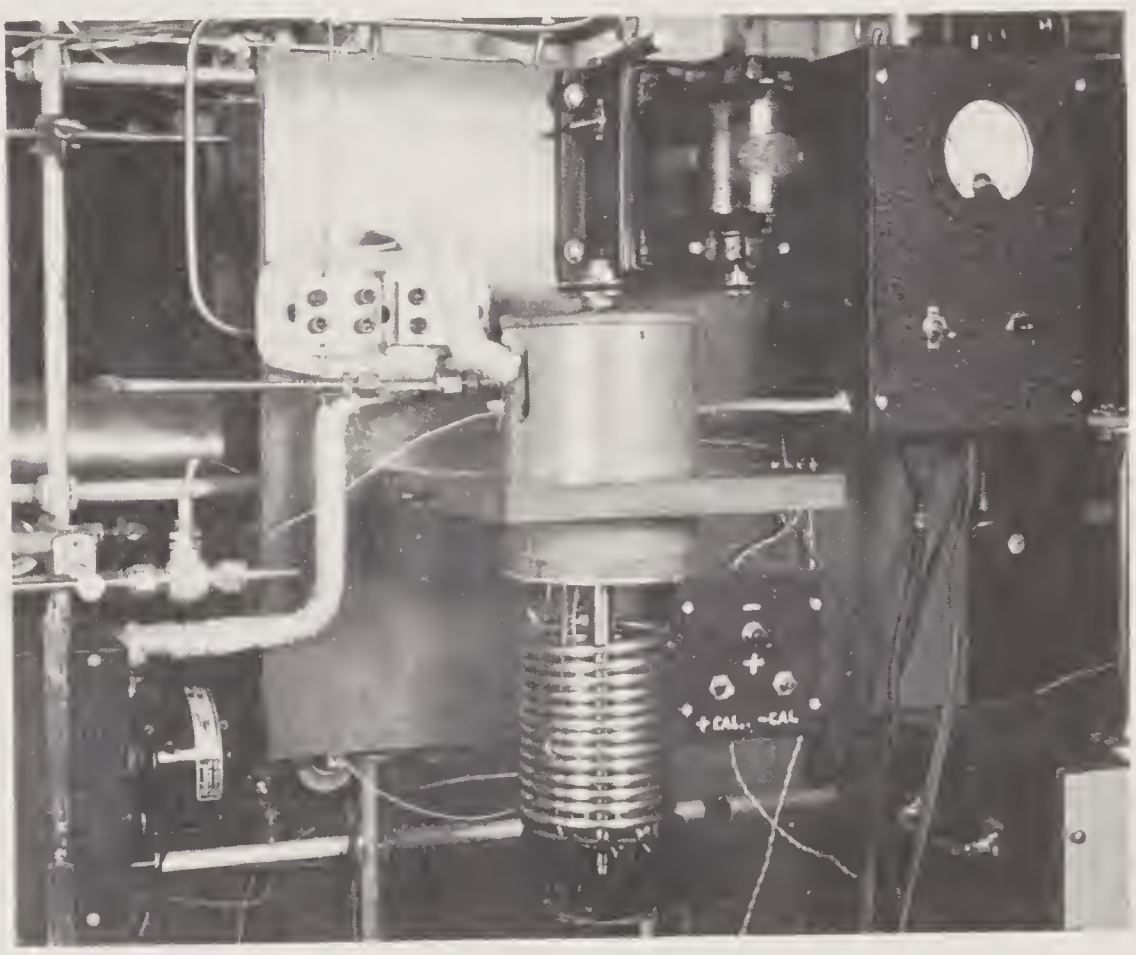


Fig. 11-6. Self heating column arrangement used for programming temperature during analysis.

consisting of a stainless steel Dewar which surrounds the assembly. A circulating fan is provided which is held on a shaft made from stainless steel tubing. The shaft is supported by two bearings located above the bath and driven by a pulley arrangement. Stainless steel construction was chosen because of its low heat conductivity. No bearing

assemblies are located within the bath, thus eliminating possible troubles with bearing lubricants which have to withstand wide temperature limits. The hollow shaft permits removal of excess refrigerants by suction. The column itself is the heater. It has an electrical resistance of approximately 2.4 ohms at 25°C, hence an applied 6 volts will furnish 2.5 amperes heating current, which is sufficient to heat the column and bath through a temperature rise of 100°C within a few minutes. One end of the column must be electrically insulated. The other end is a common ground. The insulation was achieved by inserting a length of 1/4 in. OD by 2 mm ID capillary glass tubing in the inlet line between two Swagelok fittings, using nylon or Teflon ferrules. This is shown in the photograph, Fig. 11-6. The column heating current is supplied by a filament transformer which delivers 6 volts output with an input of 115 volts AC and rated for 5 amperes capacity. A Variac transformer is used to supply the input to the filament transformer, thus providing for control of the column heating rate.

A similar coil arrangement packed with highly activated charcoal is used to purify the helium carrier gas. It can be heated in the same manner with an electrical switching circuit to apply full current to the coils. This provides for a convenient bake out. During use the coil is immersed in liquid nitrogen and effectively traps impurities in the helium. With Grade AA helium it will remain effective for several days' usage between bake out. This purification is necessary when columns are started at -196°C because impurities in the carrier gas, such as air, collect on the column while it is sufficiently cool.

Although several difficulties are encountered with programming temperature, the foregoing text has shown that most of them are easily solved. There are outstanding advantages to be realized using the technique which easily outweigh any of the other difficulties that are encountered. The ability to analyze mixtures having a wide range in boiling point is its chief asset. Fig. 11-7 is a typical example of a chromatogram obtained with the method (564). It can be seen that there is good retention for each compound with an acceptable ratio of peak height to width - in other words, there is no crowding and lack of column efficiency for low boiling fractions and no objectionable broadening and loss

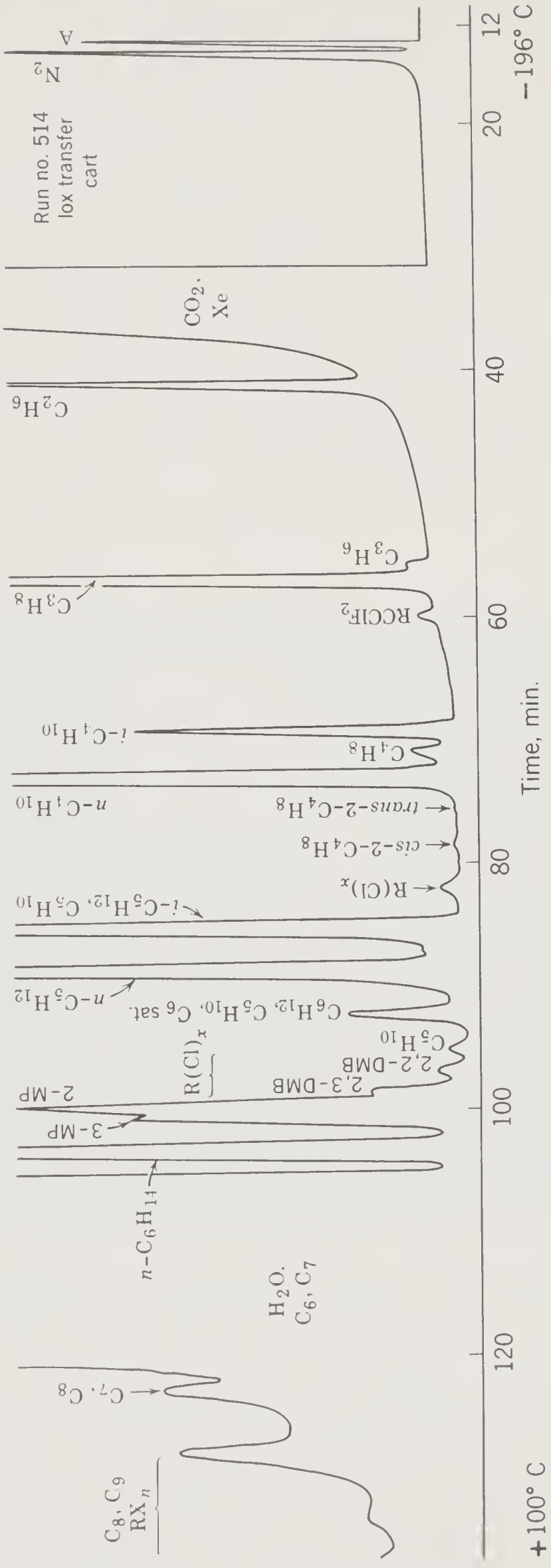


Fig. 11-7. Analysis of impurities in Aviators' Breathing Oxygen using continuous column heating.
Column: 1/4 in. x 14 ft. Carrier gas: Helium (50 ml/min)
Packing: 1.5% Squalane on 30-40 mesh Pelletex

of sensitivity for high boilers. The convenient time displacement between fractions permits easier trapping where recovery of the fractions is needed. For example, if the low boilers emerge as a series of rapid sharp spikes in a few seconds' time, it is virtually impossible to change traps quickly enough or to anticipate the location of an emerging fraction in relation to the trap and detector. Also, all fractions utilize the available number of theoretical plates with equal efficiency, regardless of their boiling point, since they undergo roughly the same history of distribution between the moving and stationary phases during their journey through the column packing.

With this technique the stationary phase is not subject to maximum temperature for extended periods of time. In practice the temperature is elevated until all sample components are driven off or until the vapor pressure of the stationary phase rises to a high enough value to cause base line drift; thus the column is automatically baked out between runs.

The use of low column temperatures permits selection of adsorbants which normally have low retention for the sample fractions. Separation at these lower temperatures avoids undesirable reactions on the column, such as deuterium-hydrogen exchange reactions, degradations, or polymerizations. If partition columns are used with this technique their lower limit of operation is just above or nearly equal to the freezing point of the stationary phase. Usually freezing of the liquid film has very harmful effects on the column efficiency, and for this reason most very low temperature work is restricted to gas solid chromatography or packings of the liquid modified solid adsorbant type.

Chapter 12

DETECTORS

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U.S. Naval Ordnance Test Station

IT MAY BE SAFE to assume that as much emphasis has been placed on the development of detectors for gas chromatography as the total time spent on all other aspects of the method. The development of reliable high sensitivity detectors has no doubt been largely responsible for the phenomenal growth of gas chromatography. Methods of detection are quite numerous, and they vary in complexity from a simple gas burette to a time of flight mass spectrometer. The sole purpose of the detector is, as the name implies, that of detection of sample constituents. It should respond continuously in a reproducible manner to changes in the composition of the eluent gas from the column without hysteresis. It should be quite sensitive to these changes and linear in response.

There are two basic types of detectors; those that respond to changes in concentration as the first derivative, i.e., differential detectors, and those that respond to the accumulative change, i.e., integral detectors. The first detectors employed were of the integral type; however, modern methods use differential detectors because of their greater sensitivity and the easier interpretation of the chromatograms obtained. For quantitative results the integral of the change in column effluent is necessary; consequently various methods have been devised to integrate the output of the differential detector. This will be dealt with later as a special problem related to detection.

James and Martin have been accused of publishing their first practical papers in obscure journals from the standpoint of general interest; however, it should be recognized that most tools of the researcher arise from acute need, and no other field is faced with such formidable analytical problems as biochemistry. Many significant advances in chromatography, even the latest super-sensitive detectors, have arisen from the efforts of biochemists, hence it is this author's feeling that the results were quite properly published in the Biochemical Journal, and the fault, if any, lies in the failure of others to notice these earlier developments in the specialized field and attach proper significance to the results. James and Martin first separated a series of fatty acids and devised a method to continuously titrate and record the appearance of the acids in the carrier stream with time. The result was an integrated record of the change in column effluent. This detector is now regarded as primitive and suitable only for materials which will ionize in solution, but it established the prime requisite for sensitive detection, i.e., that of ignoring the carrier gas completely and sensing only sample constituents. All methods of detection rely on some manner of eliminating carrier gas signal. The ultimate sensitivity is limited in part to the degree with which this is established.

The most straightforward solution to nullifying the carrier gas signal was employed by Janak (68) and Van der Craats (189). They used carbon dioxide for the carrier gas and passed the column effluent into a burette or a pressure responding device after passage through a dilute aqueous solution of potassium or sodium hydroxide, thus physically removing the carrier gas. Sample constituents were not absorbed by the caustic solution, hence they could be measured as they accumulated. A plot of volume accumulated versus time gives the typical integral form chromatogram. The method is perhaps the ultimate in simplicity and the easiest and least expensive to acquire. It is restricted to comparatively large sample sizes and materials that will not dissolve in or react with the caustic solution. Also, in its present form it requires manually recording the results. The problem of automatic recording by this method was solved by Janak (251) using a pressure responding servomechanism to collect and record the fractions. In view of

the relatively low sensitivity and the amount of effort involved to duplicate this system, such an approach is no longer justified.

DIFFERENTIAL DETECTORS

Gas Density Balance. Martin and James also receive credit for the first high sensitivity differential detector. The detector is an ingenious network of channels in a copper block (Fig. 12-1) which compares the relative densities of the measuring and reference gas using a differential thermocouple anemometer sensing device. The network of channels is mechanically equivalent to a Wheatstone bridge circuit, and has been described in terms of this analogy by Munday and Primavesi (278). At balance there is no flow through the anemometer. The device is adjusted to balance when both arms of the bridge contain only pure carrier gas.

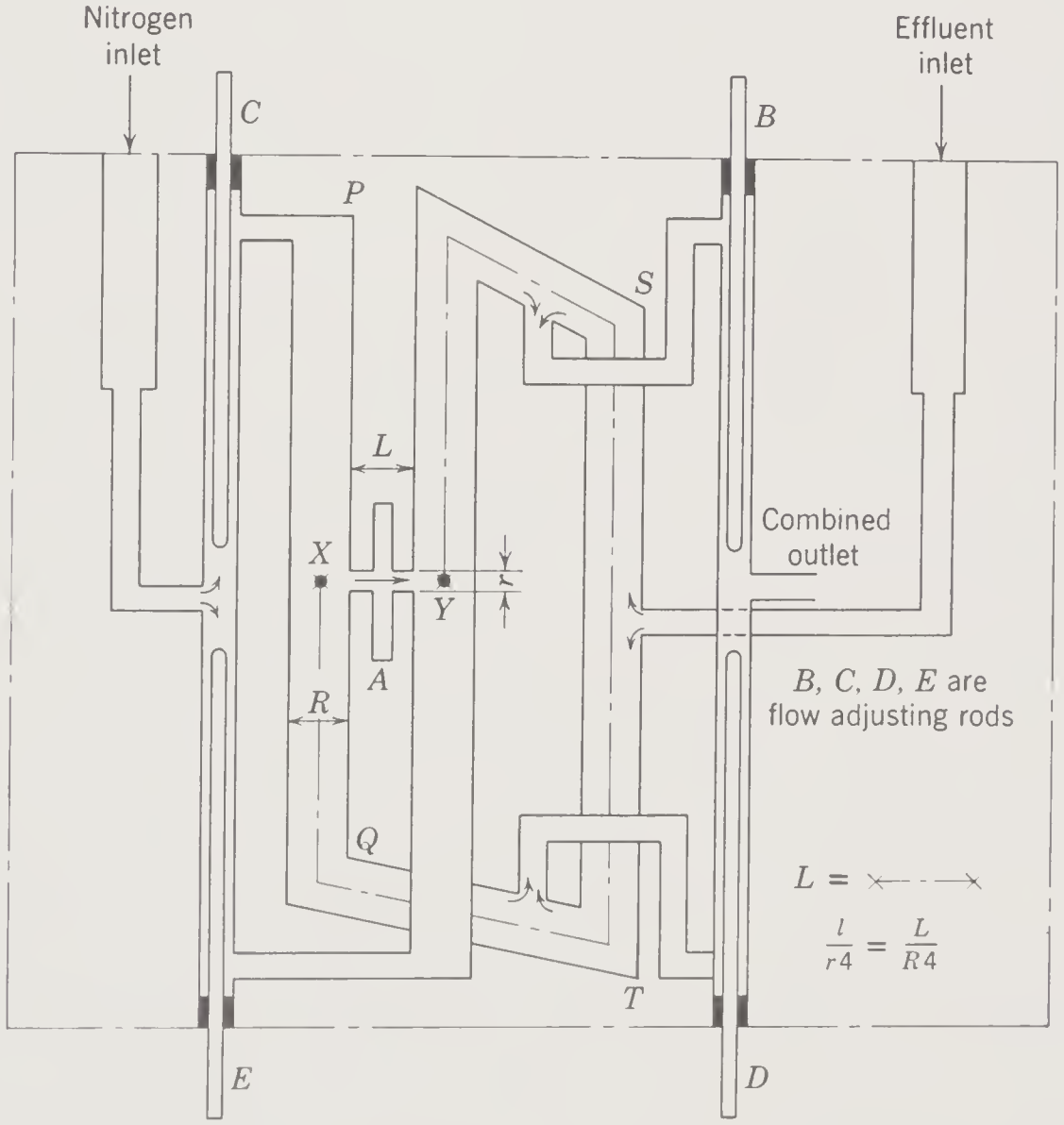

Fig. 12-1. Diagram of Martin's gas density balance. Courtesy of Reinhold Publishing Corporation (439).

When the gas in the measuring side changes in density due to a sample constituent entering the measuring side, a slight flow is set up in the anemometer which shifts heat toward one of the thermocouples at the expense of the other. A significant feature is that only pure carrier gas flows through the anemometer, thus the detector responds with very linear behavior, and its calibration (peak area) is directly proportional to the density of the sample constituent. The high price of this detector has discouraged its general usage. It is doubtful if the price will ever be significantly lowered due to the extreme difficulty in manufacturing it.

Thermal Conductivity. The method of detection most commonly used at the present time depends upon thermal conductivity changes in the effluent. Most commercial instruments use this type of detection. These detectors are easy to build and give sensitive response without the necessity of using amplifiers. Some employ hot wire filaments for sensing elements and others use more sensitive thermistors. They have a further advantage of not requiring complicated electronic circuitry unless extreme efforts are made to improve signal to noise level. In operation they are much like a Pirani gauge, but used to measure concentration changes in the surrounding gas while held at constant pressure rather than the usual application of the Pirani for measuring pressure changes. The detector in its simplest form consists of two heated sources arranged in a bridge circuit with two reference resistors and trim resistors provided for final balancing of the bridge. One source is kept in pure carrier gas and the other is placed in the column effluent stream. Thus again the principle of nullifying the effects due to carrier gas have been utilized by a cancellation arrangement. The widespread use of this detector coupled with the fact that it is the least expensive and most readily available form on the market today justifies considerable attention in the text to this method of detection.

PRINCIPLES OF DETECTION BY THERMAL CONDUCTIVITY

The sensing elements of a katharometer are heated sources which change temperature as a function of the

thermal conductivity of the environmental gas. The electrical resistance of the source is in turn a strong function of its temperature. These sources can be wire filaments such as platinum, tungsten or any wire material having a suitably high temperature coefficient of resistivity. Or they can be semi-conductors which have much higher temperature coefficients under some conditions but of opposite sign.

In order to realize optimum response characteristics, the effects due to detector geometry, block and filament temperatures, bridge linearity, current input, and the thermal properties of the environmental gas must be viewed over the wide range of operating parameters likely to be encountered. In most instances these parameters fortunately combine to give surprisingly good response; however, a critical examination reveals that the system is quite complex, and that it has very definite limitations. Some appreciation for these shortcomings will enable the worker to cope with possible difficulties he is likely to encounter, and also point out the futility of certain attractive practices that would at first appear to be fruitful.

Carrier Gas. First we will consider the environmental gas. Detection by this method depends upon thermal conductivity variations in the gas as a function of composition. Let us assume that the column is operating ideally and each sample constituent is completely separated and emerges from the column mixed only with the carrier gas. This then involves changes in the thermal conductivity of the resultant binary mixture (carrier plus pure component) as a function of composition. The subject of additivity of thermal conductivities of binary gas mixtures has been of considerable interest over a number of years, and it is well known that the additivity is not a linear function with composition. Also, the thermal conductivity of a binary mixture can change in a surprising way with temperature and with carrier gases which have conductivities not too different from the sample constituents. Peak inversions can occur due to a change in sign between the relative conductivities of the carrier gas and of the mixture under measurement. The effect was discussed by Bohemen and Purnell (541) in the special case of nitrogen carrier gas with various light hydrocarbons. In general, this trouble can be avoided by choosing a carrier

gas of much higher conductivity than the sample constituents. This not only eliminates peak reversal problems, but provides some gain in sensitivity as well. In the United States helium is a popular choice since it has a very high conductivity, it is non-reactive, and does not interfere with subsequent analysis of recovered gas chromatography fractions.

Some countries cannot readily obtain helium; therefore they must choose some other carrier gas. Hydrogen compares favorably with helium in having a very high conductivity, but there seems to be some reluctance to use it with katharometer detection because it is potentially reactive with the materials in the column. Furthermore, it offers some explosion hazard. Nitrogen has been commonly employed as a carrier gas in the United Kingdom countries. Its thermal conductivity is much closer to most compounds of interest, hence there is a sacrifice in detector sensitivity with its use. The sensitivity change, however, is not directly proportional to the ratio of thermal conductivities of the carrier gases as might be supposed. For example, the ratio of conductivities of helium over nitrogen is about 6 at 0°C, which would predict a gain in sensitivity of this magnitude when using helium in place of nitrogen. In actual practice gain factors of about 2 or 3 can be realized. The explanation for this is due partly to the effect of the higher thermal conductivity upon the lowering of temperature difference between the source and the detector wall.

Detector Noise. Noise sources commonly encountered with katharometer detection are thermal convections around the filament, improper flow control around the filaments (turbulence), vibrations, stray electric signals or improper shielding and grounding, electronic noise from power supplies, and temperature variations in either the detector block or components of the associated electric circuitry. In the latter case it is important to design the circuit around the components having very low temperature dependence. Many detectors employ external reference resistors and trim resistors in portions of the Wheatstone bridge circuit exposed to ambient temperature. Special care must be exercised in the choice of these components, not only from the standpoint of materials and construction, but in their physical arrangement. Reference resistors should be

made of the best quality low temperature response resistance wire annealed after winding, and placed in close proximity to each other on a massive metal core having a high thermal conductivity. Another satisfactory arrangement utilizes four sensing elements which make up all four arms of the bridge circuit. These are arranged in push-pull with the measuring arm resistors and reference resistors on diagonally opposite legs of the bridge. Since no external resistors are needed the external circuit design is simplified. This is a feature of many commercial detectors. Thermistor detectors usually employ reference resistors but are wired within the detector block so that they are thermostated with the measuring elements. Any of these methods are suitable from the standpoint of noise suppression.

The mechanical noise encountered in detectors arises from vibration of heated elements. With long straight wire filaments this is particularly troublesome. Earlier models used weight loading or spring tensions to keep the wires taut. Modern filament detectors use wire such as kovar or tungsten wound into compact coils. This improves rigidity and at the same time reduces internal dead space. It also permits easy replacement since they can be mounted on insulated threaded inserts. Thermistors are small beads of semiconductor material and they are mounted in a similar fashion.

Thermal noise is eliminated by carefully thermostating the detector assembly. This can be done in the same thermostat used for the column or in a separate one. The use of metal blocks for the detector body serves to distribute heat uniformly throughout the detector system and prevents momentary gradients around the filaments. The use of low heat conductivity materials around the filaments such as glass has proven very unsatisfactory.

Electrical noise is perhaps the most troublesome to overcome. The power supply used must be selected with great caution and batteries, if used, must be kept in a good charge condition. For critical suppression of noise careful attention must be given to shielding and grounding of the components.

Circuit Design. There are several bridge arrangements that can be employed with thermal conductivity detec-

tors. Four examples are given in Fig. 12-2 by Dimbat et al. (198). These authors recommend arrangements B and D using relatively high external reference resistors in order to minimize current changes in measuring elements. A typical circuit diagram is given in Fig. 12-3.

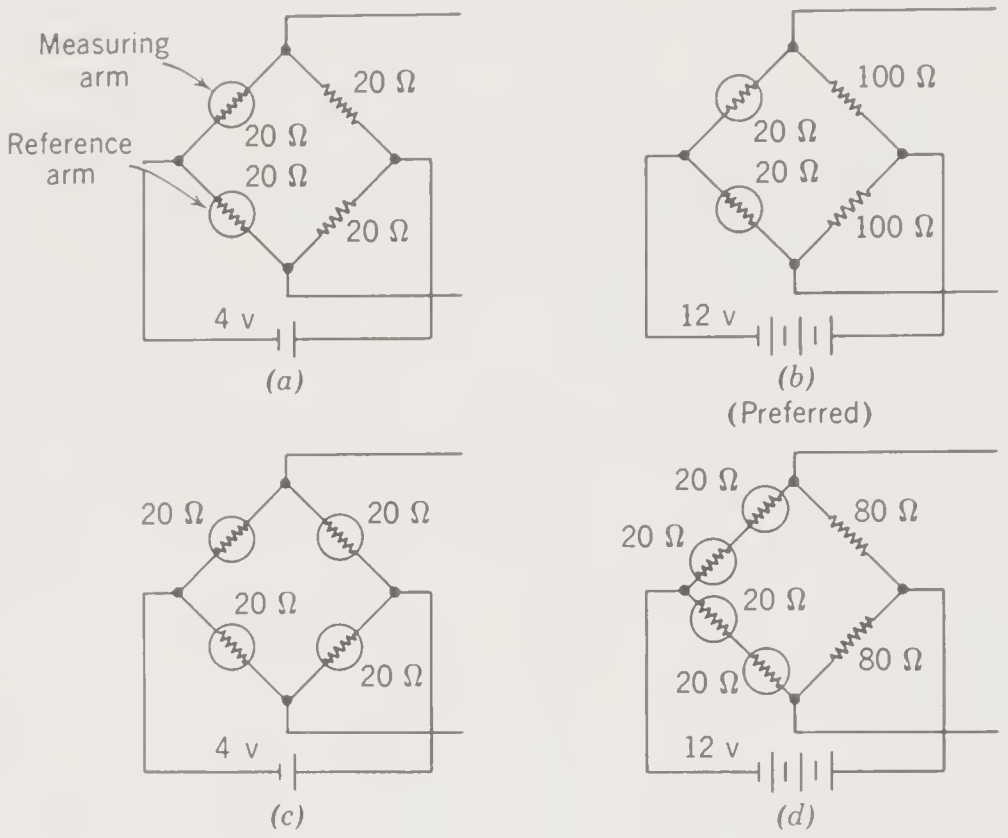

Fig. 12-2 Wheatstone bridges for two and four cell thermal conductivity detectors. Courtesy of Analytical Chemistry (198).

Considerable attention has been given to proper circuit design by the various manufacturers of detector systems and optimum circuit requirements are dependent upon many factors such as cell geometry, resistance values of the elements, operating temperatures and current requirements, column performance characteristics, recorder impedence, recorder span and recorder speed. Most of these involve electronic theory which is beyond the scope of this text; however, in general these properties must be chosen to allow as nearly as possible a detector response that instantaneously and reproducibly follows changes in the composition of the column effluent as a direct linear function of composition. This requires that the thermal conductivity is also a linear function of composition which in the case of dilute concentrations of, for example, hydrocarbons in

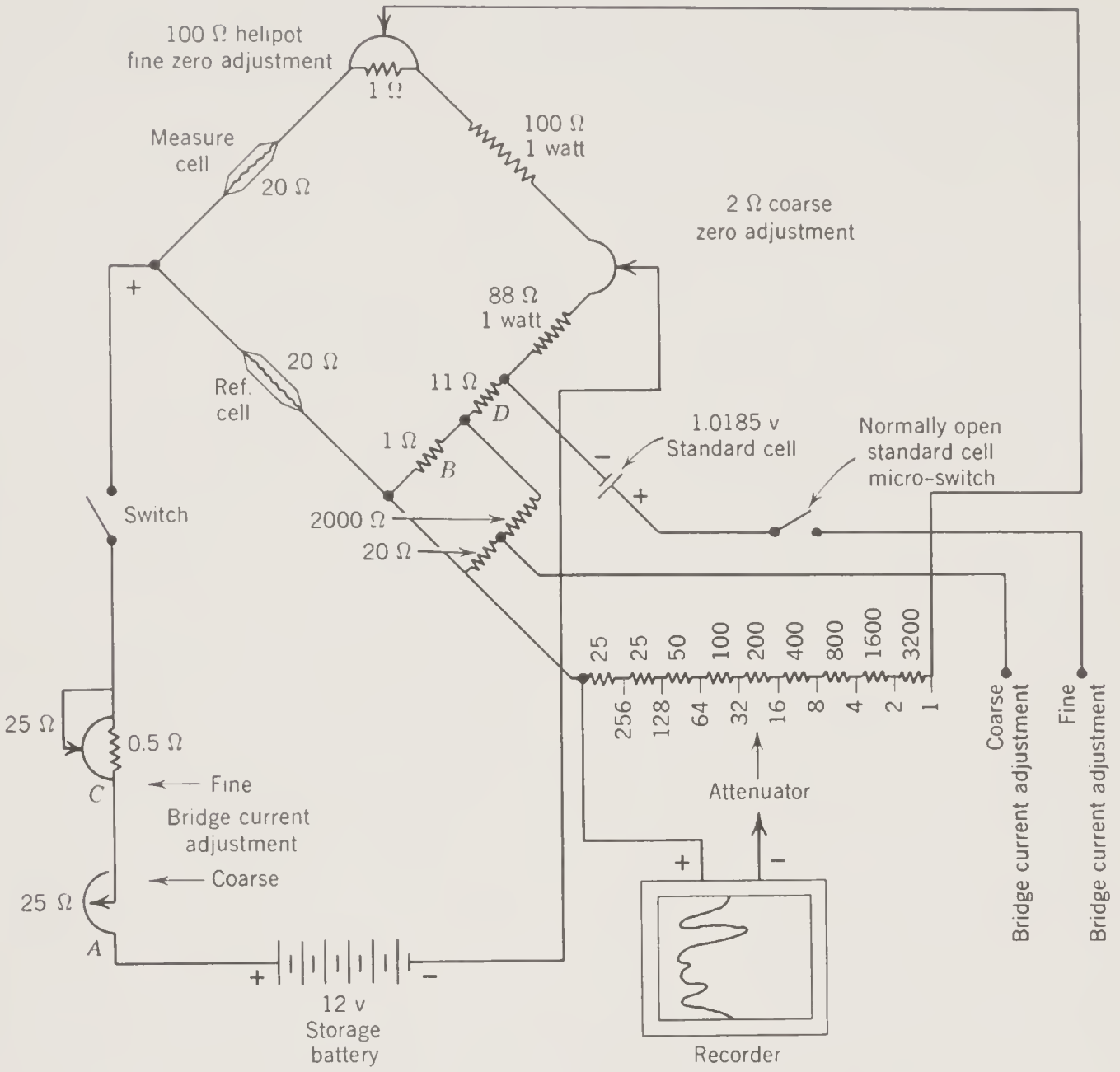

Fig. 12-3. Schematic wiring diagram for 12 volt 200 ma. bridge for thermal conductivity detector. Courtesy of Analytical Chemistry (198).

helium, is a resonably valid assumption.

DETECTOR SENSITIVITY

Most workers feel a need for adequate comparison between the various models and types of detectors available today. There have been some attempts made to provide for a common basis for comparison, perhaps the most notable being the sensitivity parameter proposed by Dimbat et al. (198).

$$S\ (\text{ml} \times \text{mv per mg}) = \frac{A \times C_1 \times C_2 \times C_3}{W}$$

where S = sensitivity parameter
A = peak area, sq. cm
C_1 = recorder sensitivity, mv per cm of chart
C_2 = chart speed, min per cm
C_3 = flow rate at exit of column, ml per min, corrected to column temperature at atmospheric pressure.
W = weight of component, mg

Recently the author conducted a survey of the leading suppliers of gas chromatography equipment known to him, and requested performance data and other related characteristics of their various detectors in the above units. It soon became apparent that such a comparison was relatively crude because the value S as determined by this means depends upon several other factors not taken into consideration. The most important of these are: the effect of the nature of the compound under detection (i.e., molecular weight or structural effects), the choice of carrier gas, and the associated circuitry. As a result this parameter was ignored by most companies or answered with reservations. The response characteristics for several different compounds are given in terms of this parameter in Fig. 12-4 for a sensitive thermistor detector (639).

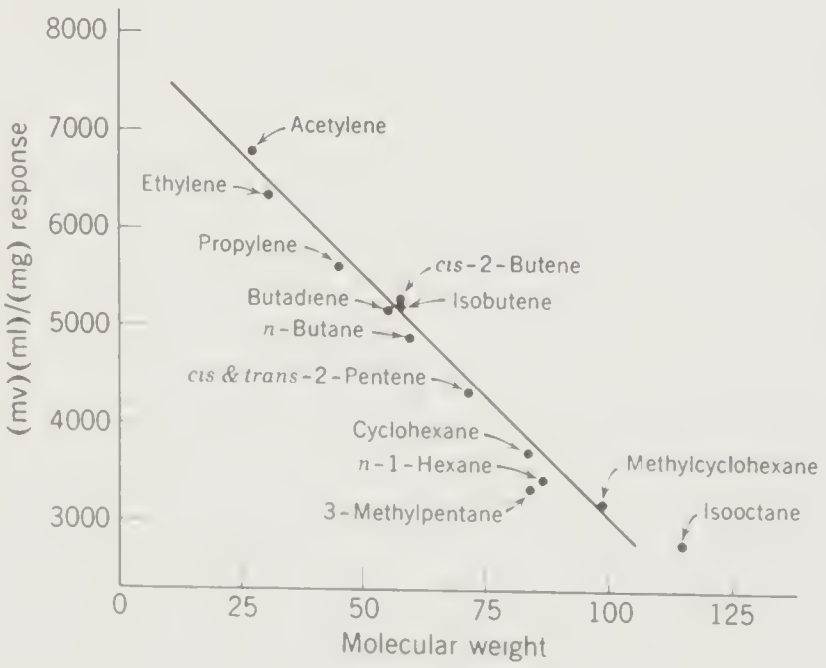

Fig. 12-4. Response characteristics of a thermistor type thermal conductivity detector. Thermistors 8-10,000 ohms at 25°C. Temperature, 22°C. Courtesy of Loe Engineering Company.

For filament detectors values up to 1500 are reported for compounds of this class where bridge voltages of the order of 12-13 volts DC are employed and helium is employed as the carrier gas. Although rough comparisons between thermal conductivity detectors and others such as the Martin density balance can be made by use of this parameter, it is pointless to use it for evaluating the more recent supersensitive detectors. With these detectors the above criticisms apply even more strongly since their output can change exponentially with some of the factors not taken into consideration. There are indications that under specific conditions these detectors will provide S parameters of the order of 10,000 or higher.

Detection Limits. The least discernable signal from a sample trace above the inherent background noise is the sensitivity limit. This term is usually expressed in parts of component (taken at unity) per parts of carrier gas, and it is useful in that it places the lower limit on the amount of material needed for a significant measurement. For accurate work it is obvious that one should work with sample sizes sufficient to give response considerably above this limit.

Molar Response Characteristics. The relative response of both filament and thermistor detectors using helium gas has been measured for a variety of compounds against a standard measured response from benzene (486, 686):

It was shown that there exists a linear molar response within a homologous series, and that the relative response is the same for both thermistor and filament conductivity detectors.

For quantitative work these linear relations can be used instead of direct calibration. In practice the response for any compound of known molecular weight and structure can be predicted from the measured response to benzene provided the slope of the molar curve is known and at least any one compound in the particular homologous series is known relative to benzene.

In principle this property could also be used to assist in structure or molecular weight determinations. (See

Chapter 13).

TIME CONSTANT

One of the most important parameters of detector performance is its time constant. Ideally the detector should respond at an infinite rate to changes in the composition of the effluent gas. Although this cannot be achieved it is possible to build detectors with rapid enough response to introduce no significant errors in the display of the elution peak. This is done by keeping internal passages small, using low heat capacity sensing elements, and providing for rapid exchange of the effluent gas entering and leaving the region surrounding the sensing elements. In designing detectors for low time constants the sensitivity of the elements to changes in carrier gas flow must be minimized in order to reduce noise or base line drift due to flow variations. This requires some compromise in design between an arrangement where the gas stream passed directly over the elements or enters the chamber containing the elements by diffusion. Fig. 12-5 is a schematic representation of these detector designs (198). Detector A is a direct pass type with a low time constant but with objectional flow sensitivity. Detector B is a diffusion type having low flow sensitivity but too long a time constant. Detector C is a compromise arrangement which satisfactorily approaches the time-sensitivity requirements. One of the best solutions to this problem is the Gow-Mac Pretzel design, Model 9285, which divides the gas stream equally between parallel passages and places the sensing elements in connecting tubes between these passages.

The carrier gas flow rate largely determines the time constant and flow sensitivity; however, this rate is determined by column performance requirements, rather than detector requirements. For this reason detectors must be designed for specific flow rates. For large column work requiring excessively large flow rates a bypass arrangement can be provided to shunt only a small portion of the measuring gas through the detector. Perkin-Elmer Vapor Fractometer models employ this technique with their preparative scale columns, thus utilizing one detector for widely varying flow conditions.

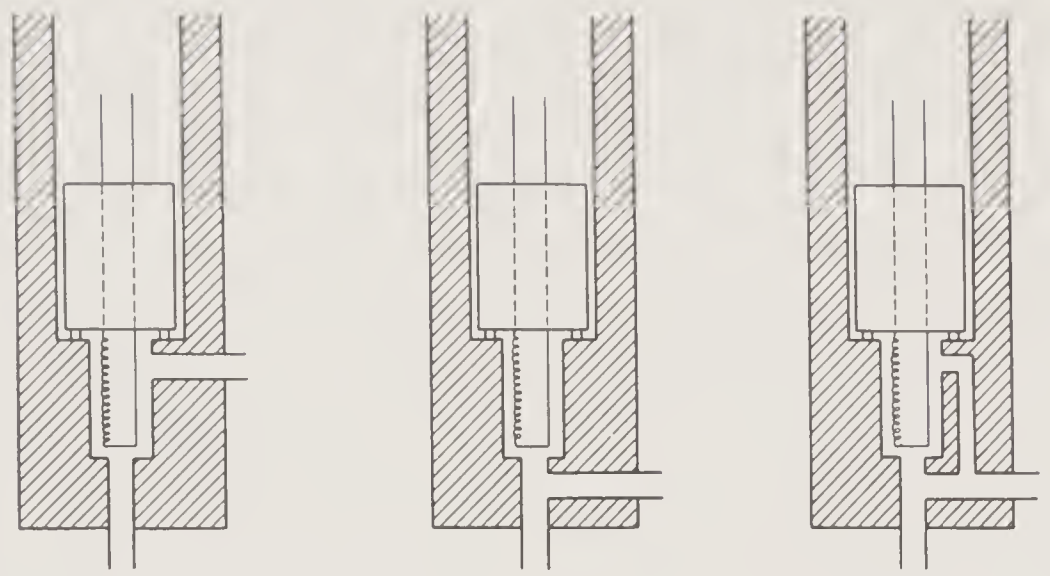

Fig. 12-5. Thermal conductivity cell designs. Courtesy of Analytical Chemistry (198).

A. Flow through cell	B. Convection-diffusion cell	C. Self-purging cell
Time constant. 1 second	Time constant. 20 seconds	Time constant 10 seconds
Flow sensitivity. 1 μv. per ml. per minute change in one cell	Insensitive to flow changes	Insensitive to flow changes

Schmauch (692) has recently studied the effect of detector response time and flow sensitivity upon the adequacy of representation of column resolution in a chromatogram. He used a mathematical model of a chromatogram band in addition to experimental approaches to show a quantitative relation between band shape and the ratio of response time to band width. He has shown that for adequate representation of a band the ratio of response time to band width must have a value of 0.2 or less. In this work he expresses response time in the conventional manner; the time in seconds required for the detector to respond to 63.2% of the ultimate output caused by a sudden transition to a differential but fixed concentration of a binary mixture entering the inlet of the detector. He uses a measure for band width which is somewhat unconventional in chromatography work,

but nonetheless valid for the purposes of his mathematical model. It is one-half the band width at 60.7% of maximum and is, in fact, the standard deviation term, σ, of the equation for a normal distribution curve.

DETECTOR SENSITIVITY AND COLUMN PERFORMANCE

It has been clearly demonstrated that column performance is enhanced by using smaller sample sizes. Also, column efficiency is improved by reducing column diameter as well as increasing column length, but diameter reduction also requires sample size reduction because of the resultant decrease in plate capacity per unit length of column. The limiting sample size is dictated by the sensitivity limit of the detection system, and as a result a large amount of effort has been devoted to increasing detector sensitivity. There are some commercial detectors on the market using thermal conductivity which have very sophisticated engineering to suppress background noise, thus permitting a higher signal to noise level. Most modern instruments possess these features to some extent. The highest sensitivity claimed at this time for thermal conductivity detection is one part component in 10^7 parts carrier gas. This detector is marketed by Barnes Engineering Company, and uses flake thermistor sensing elements in conjunction with careful thermostating of cell temperature.

SUPER SENSITIVE DETECTORS

The difficulties encountered in pushing thermal conductivity detectors to greater limits has reached a point where further development is not practical. Recently new detection principles have been discovered which have completely revolutionized the analytical capabilities of the method. Almost concurrently with the development of such detectors came the introduction of capillary columns by Golay (395, 577). With such columns efficiencies of 200,000 theoretical plates have been obtained and the necessity of using microgram quantities of sample mixtures also requires detection in the super sensitive range.

The forerunner of these detectors was a simple glow discharge ionization device described by Harley and

Pretorius (229). In general, these detectors all employ changes in the electrical conductance of the effluent gas brought about by various methods of ionization. The Harley-Pretorius model produces the ionization by applied DC potential between two electrodes. The sample constituents entering the detector admixed with carrier gas produce very large changes in ion concentrations, hence very large changes in electrical conductance can be realized. High signal to noise ratios can be readily achieved. These detectors give varying amounts of success depending upon conditions of cleanliness, current and voltage applied, and the nature of the carrier gas used, and the type compounds being measured. In general, their characteristics seem to vary rapidly with use, obviating their application to quantitative work. Pitkethly (632) described a rather successful version, using a pair of neon glow bulbs arranged in a bridge circuit. He outlined conditions required for reproducible results, and although his model met with some success, it proved troublesome compared to the more recent types.

Ryce and Bryce (490) adapted the ionization pressure gauge in an ingenious manner. They chose helium for the carrier gas because of its high ionization potential, i.e., 24 volts DC. They operated the tube at an applied potential of 18 volts which was ample to ionize any materials commonly encountered, but low enough to prevent ionization of the carrier gas. In this way the current output of the tube was due almost entirely to the ionization of the sample molecules. Since this device relies upon thermionic emission it is sensitive to changes in the emission characteristics of the filament. Also, the tube was necessarily operated in a region where the output efficiency was quite sensitive to changes in the filament current, thus requiring a self-regulating current supply. Quantitative accuracy is not easy to obtain under these conditions. It is doubtful if this method was ever developed to give performance which was as reliable or as sensitive in response as the two more recent Lovelock (613) or McWilliam and Dewar (619) ionization detectors. Lovelock developed an ionization detector using a different method of ionization. This detector uses a radioactive source with argon carrier gas. The argon is excited to its metastable state by beta radiation from the source which has a

strength of about 80 millicuries. The source can be either radium or strontiom-90, the latter being more desirable. The excited argon does not ionize, hence, with an applied potential between an anode and cathode up to 2-3000 volts there is essentially no current produced by the carrier gas. When an ionizable substance enters the detector there is an energy transfer from collision with metastably excited argon atoms to produce ions which are in turn accelerated to the cathode by the applied potential. The amount of current so obtained is dependent upon the applied DC potential, thus the sensitivity of the detector can be changed over very wide limits. With high molecular weight compounds sensitivities of over 100,000 times that of conventional thermal conductivity detectors have been realized. This highly successful system is rapidly appearing on the market by numerous instrument companies. The sensitivity of the Lovelock detector is quite high for large molecules, but for hydrocarbons under molecular weight 100 and many inert or permanent gases the sensitivity falls off very rapidly. It is almost completely insensitive to air, for example.

Recently Lovelock (612) published some details of his detector designed specifically for use with Golay columns. He considerably reduced the internal dead space, thus achieving an acceptable time constant for column flow rates of the order of 1 ml per min. This detector permits usage of capillary columns with 1-3 microgram size samples and column efficiencies of 200,000 theoretical plates have been achieved (699).

FLAME DETECTORS

A very simple detection method is based on the temperature changes of a hydrogen flame measured with a thermocouple located in the flame tip (301, 324). The hydrogen feeding the flame is combined with effluent gas from the column. An instrument using this principle is now commercially available with a claimed sensitivity of about ten times greater than conventional thermistor type thermal conductivity cells.

This method has been used quite successfully for a number of years by Desty and co-workers at the British Petroleum Institute, but the method seems to have enjoyed

little appreciation in the United States because of the reluctance to use hydrogen, and perhaps a general distaste for burning the separated fractions in a flame.

FLAME IONIZATION DETECTOR

Probably the most sensitive detector yet devised was introduced in its infant form by Pretorius. He used a hydrogen flame detector, but measured instead the electrical conductivity of the flame by inserting two electrodes in the flame with an applied voltage of around 150.

McWilliams and Dewar later described a much improved model using two flames, one in reference gas and the other in the column effluent in which the respective electrodes were incorporated into an electrometer tube bridge circuit operating at 500 volts DC. Further gain in signal to noise was achieved by diluting the flame gas (hydrogen) with large amounts of nitrogen. Several instrument companies are currently developing this promising method. The first one appearing on the market was recently announced by Perkin-Elmer Corporation. This detector offers higher sensitivity in the lower molecular weight range than the Lovelock detector, and is particularly suitable for capillary columns because it has essentially no dead space. The column effluent is fed directly into the hydrogen-nitrogen blend feeding the flame.

The excellent merits of this system can be appreciated from Fig. 12-6 which shows the separation of the nine isomers of heptane from a 2 microgram sample.

This chapter does not pretend to cover all methods of detection that have been used, but rather covers most of the forms which have enjoyed widespread recognition and those leading to the development of the more recent types. There are many ways of looking at a mixture of gases appearing at the exit end of a column, and certainly any property of this mixture which changes as a function of composition could be adopted for measurement purposes. The passage of the gas stream into such instruments as infrared and ultra violet absorption spectrometers, mass spectrometers, nuclear magnetic resonance spectrometers, emission spectrographs, etc., are finding important use for specialized work in gas chromatography. In general, these

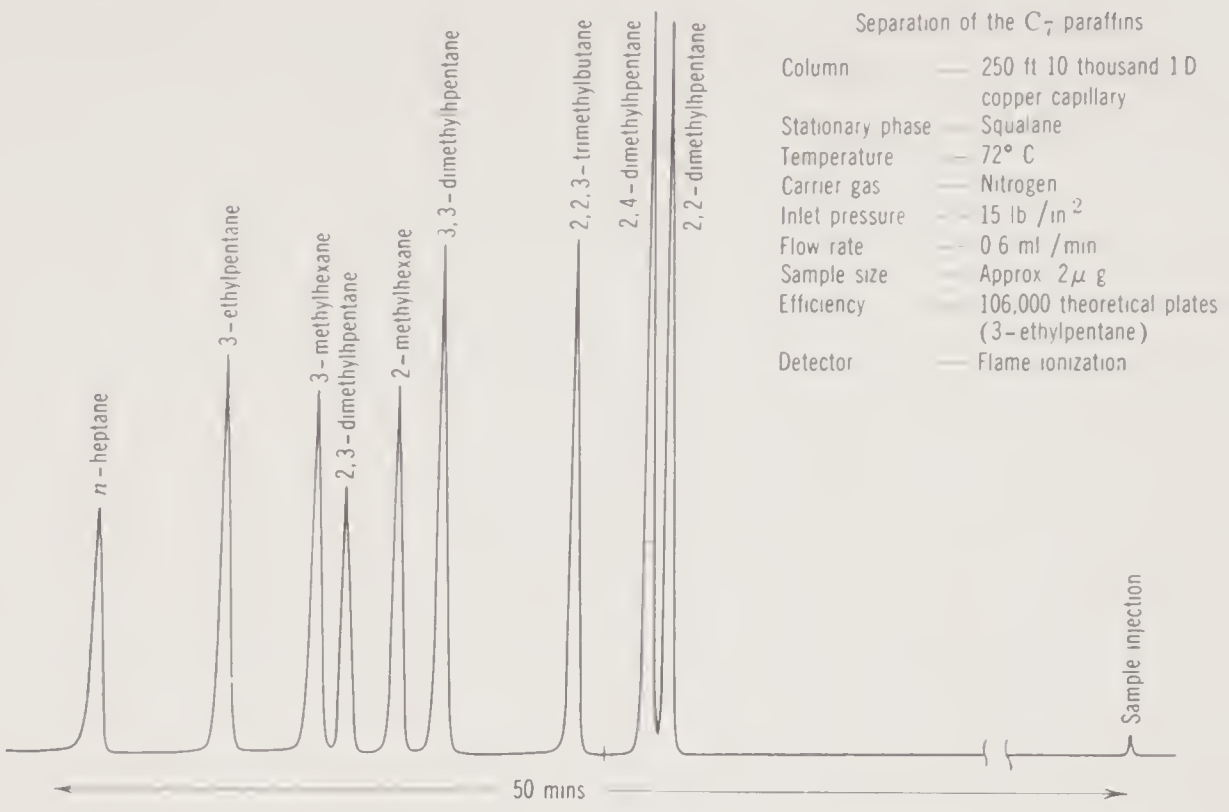

Fig. 12-6. Separation of the C_7 paraffins. Courtesy of Desty, British Petroleum Institute.

instruments lack sufficient sensitivity to allow their direct application in the sense that a detector is used. Most laboratories recover the separated fractions by condensation from the exit carrier gas and submit the recovered fraction to such instruments for additional study. For work with material involving isotopic tagging the combined use of gas chromatography with mass spectrometry offers an extremely useful combination (206).

INTEGRATION

Differential detectors display each fraction as a peak which represents the change in composition in the binary mixture, carrier plus sample component, with time. The area under this peak (above base line) is directly proportional to the amount of component producing the signal. Methods for integrating chromatography peaks are quite numerous and an extensive treatment of this subject is beyond the scope of this book. Since detector output is involved, integrations can be considered as part of a detection system designed to display the chromatogram on a numerical basis.

Since strip chart recorders are commonly employed to display detector output they can be adapted to furnish the peak integral. A variable drive output can be attached

to the slide wire capstan so that at base line an output shaft has zero rotation, but the shaft rotation increases in a direct linear relation to the amount of deflection above base line. This shaft then drives a counter or pipping pen arranged to record along the edge of the chart. The counter reading or the number of pips observed during the passage of a peak is the integrated value. Ball and disc integrators have been used for this application.

Other methods use electronic instruments which couple directly to the detector output or derive their emf signal from an extra slide wire in the recorder. A suitably designed Watt-hour meter can be used in this manner.

The author uses an electronic integrator which amplifies the detector output with a chopper stabilized DC linear amplifier and feeds the signal to a condenser whose charge build-up can continue until it reaches a potential sufficient to fire a tube. When the tube becomes conducting it discharges the condenser. The rate of tube firing depends upon the detector output emf and each tube pulse trips an electronic counter circuit. Provision is made to zero the count rate for base line and clear the counters between peaks. Such a system is not dependent upon the recorder span, and thus eliminates the necessity for keeping large peaks within the recorder scale. Most suppliers of gas chromatographs can supply either their own integrating system or one modified for use with their instruments.

Chapter 13

ANALYTICAL METHODS

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APPLICATIONS OF GAS CHROMATOGRAPHIC METHODS now run into the hundreds and a critical review is no longer within the scope of a single author. A literature search is already time consuming even for a specific application. The bibliography in Appendix II, which includes titles of papers, should be of considerable assistance in this regard.

In this chapter we shall be concerned with a general approach to the kinds of data usually obtained and the methods used to arrive at useful results. Although gas chromatography is primarily a qualitative and quantitative analytical technique, this by no means exhausts the scope of the method. In addition, gas chromatography offers many possibilities for studying properties of solutions, the thermodynamics and mechanisms of adsorption and absorption, and the properties of surfaces.

GAS CHROMATOGRAPHIC DATA

Information from the Detector. Although it is customary to record the detector signal with a recording potentiometer, certain integral detectors do not require a recorder. For example, if carbon dioxide is used as a carrier gas, a gas collecting buret filled with potassium hydroxide solution serves as the detector and it is necessary to read the buret only at intervals. Even with a differential detector,

a very few carefully selected observations of the detector response may serve the purpose for specific routine applications. In general, however, it is necessary to follow the detector response continuously over a period of time and the attenuated or amplified signal is recorded on a strip chart recorder.

The only data obtained from the chromatograph is a recording of detector signal versus time. For many purposes the time is a convenient variable. If the flow rate is known and constant, the time can be easily converted to volume of carrier gas passed through the system. On the other hand, the detector signal (position of the recorder pen) is seldom a simple function of concentration of a component in the carrier gas. Various methods of interpreting the signal in order to obtain quantitative results will be considered.

Other Information. The amount of additional information required varies with the detector, the method of obtaining analytical results, and the nature and accuracy of the results expected. It may be necessary to obtain any or all of the following information: nature of column packing, type and amount of liquid phase, density of liquid phase, nature of carrier gas, inlet and outlet pressures, flow rate, column and detector temperatures, volume of dead space in various parts of the system, interstitial volume in the column, and perhaps the history of the particular column.

QUALITATIVE ANALYSIS

Gas chromatography is primarily a method for performing separations. Provided that the separation is satisfactory, any suitable method can be used to identify the pure components emerging from the column. Martin (456) has suggested that the gas chromatograph might perform preliminary separations and then, acting as a master control, send fractions out to other slave machines for detailed analysis. This is not a simple problem because only small samples are used and the components are highly diluted with carrier gas. Infrared and mass spectroscopy have often been used for identification. The method then loses the advantage of simplicity and low cost. Other methods such as radioactivity may be applicable in special cases. For many

substances the human nose is an excellent and extremely sensitive detector. A number of techniques for obtaining identification from chromatographic information alone will be considered next.

Use of Standards. In this method, the retention times (or volumes) of the unknown peaks are compared with the retention times of known pure compounds. The experimental conditions must be identical or appropriate corrections applied. Alternatively, a known compound suspected to be present in the unknown can be added to the sample. The chromatograms taken before and after the addition are compared for the presence of a new peak or the enhancement of one already present. Identical retention times are not proof of the identity of two substances unless the behavior can be reproduced with a number of different column materials at different temperatures. Furthermore, while this technique is simple in principle, it requires some knowledge of the possible constituents and a large collection of pure samples.

The use of partition coefficients or specific retention volumes eliminates the requirement that the knowns and unknowns be run under the same conditions. These properties depend only on the nature of the component, the column material and the column temperature. Therefore literature values can be used with any apparatus and only the temperature must be reproduced. Unfortunately only a limited amount of such data is readily available. We can hope that extensive tables will be collected and published, in fact the JOURNAL OF CHROMATOGRAPHY is now including Tables of Retention Volumes as a regular feature.

Retention Volume Plots. It is frequently possible to separate components by class either by gas chromatography or preliminary chemical methods. Within a homologous series, retention time increases with molecular weight. For many series a plot of the log retention volume versus number of carbon atoms yields a straight line, excluding the lowest members of the series. Data plotted in this form, as shown in Fig. 13-1, are valuable in identifying unknown components. A few members of the series establish the relationship which can then be extended to cover the remaining homo-

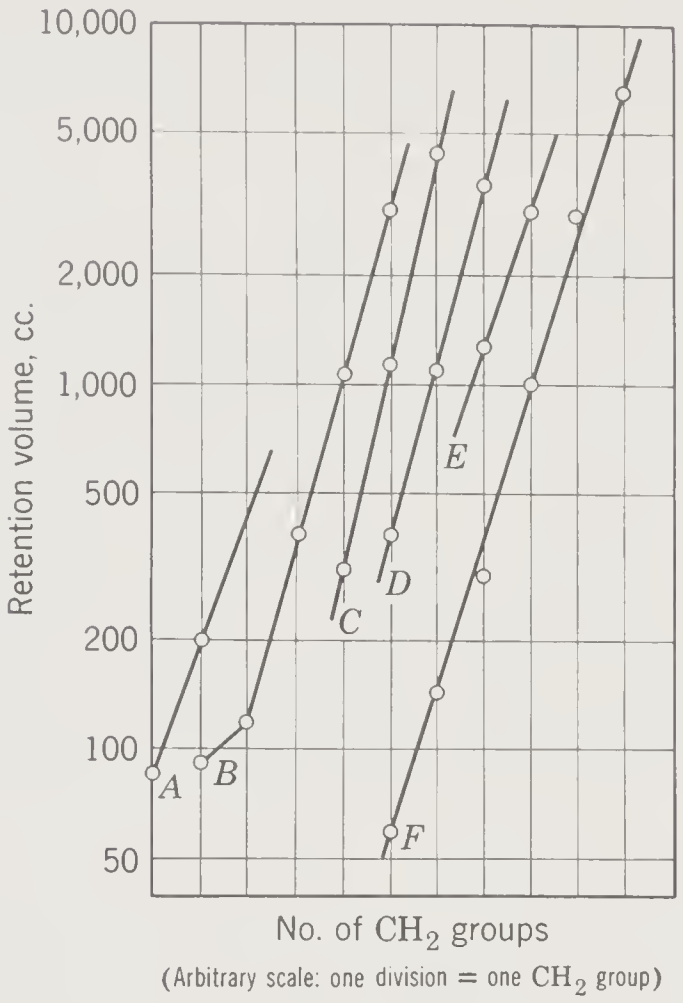

Fig. 13-1. Retention volume against number of carbon atoms on a column of dinonyl phthalate. Courtesy of Journal of Applied Chemistry (98).

A. Paraffins, $n\text{-}C_5H_{12}$ - $n\text{-}C_7H_{16}$

B. Alcohols (normal), CH_3OH - $n\text{-}C_5H_{11}OH$

C. Formates, $HCO_2C_2H_5$ - $HCO_2C_4H_9$

D. Acetates, $CH_3CO_2CH_3$ - $CH_3CO_2C_3H_7$

E. Propionates, $C_2H_5CO_2CH_3$ - $C_2H_5CO_2C_2H_5$

F. Methyl ketones, CH_3CHO - $n\text{-}C_5H_{11}COCH_3$

logues within reasonable limits.

In Fig. 13-1 a retention volume of 1000 cc corresponds to several compounds of differing numbers of carbon atoms in the several series plotted. Unless the compound can otherwise be classed in a definite series or its carbon number determined independently, the identification from

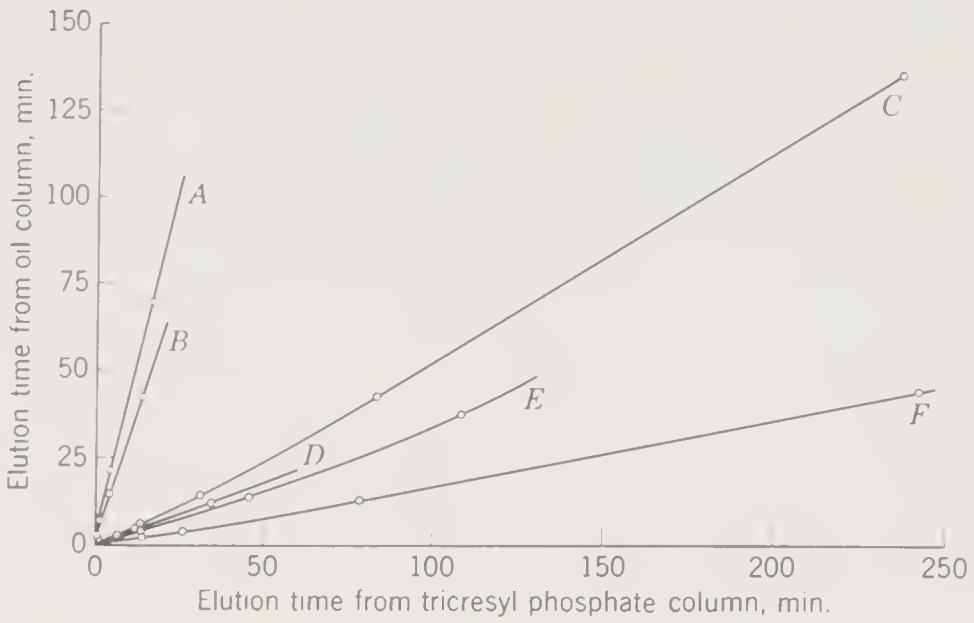

Fig. 13-2. Linear relation of retention times. Courtesy of Analytical Chemistry (263). A. Alkanes, B. Cycloalkanes, C. Esters, D. Aldehydes, E. Ketones, F. Alcohols.

from the retention volume alone is ambiguous. In this event it is necessary to use a second column with a different stationary phase, yielding another pattern of retention volumes versus molecular weights. In order to facilitate comparison, the retention volume on one column is plotted versus the

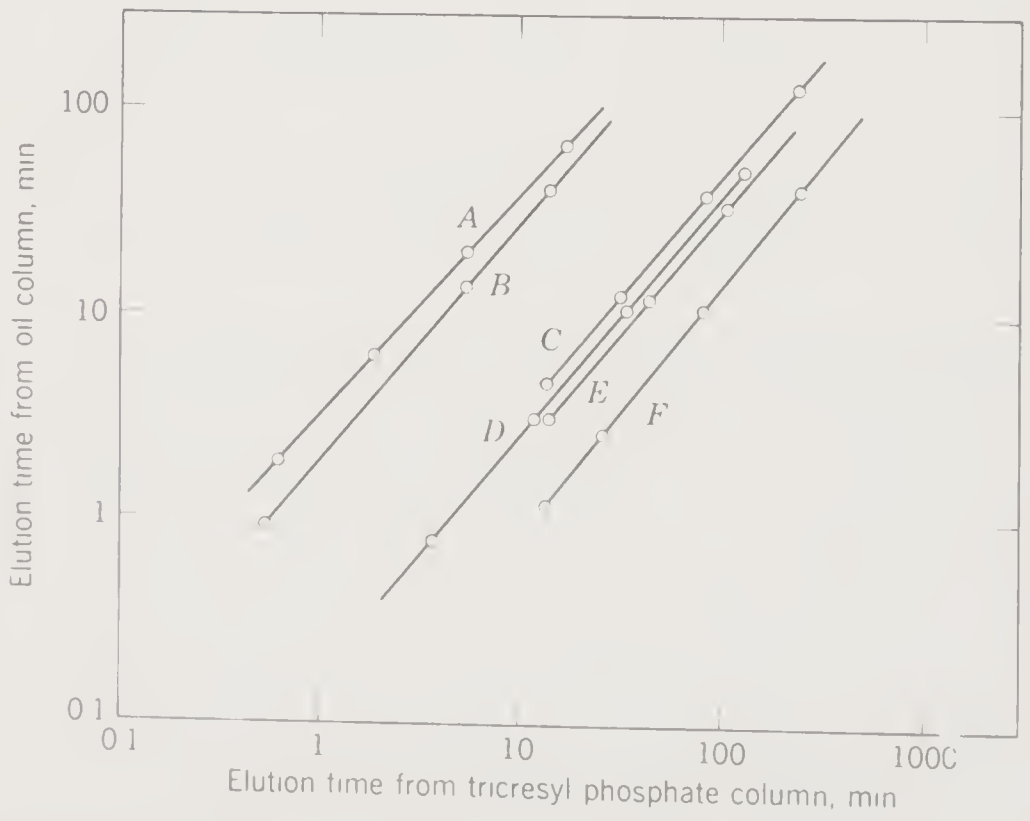

Fig. 13-3. Logarithmic relation of retention times. Courtesy of Analytical Chemistry (263). A. Alkanes, B. Cycloalkanes, C. Esters, D. Aldehydes, E. Ketones, F. Alcohols.

retention volume on the second column. Fig. 13-2 is an example of this type of plot from which identification is reasonably certain. The slopes of the lines are characteristic of each class. The log-log plot shown in Fig. 13-3 is more convenient. Here the intercept is characteristic of the class. Obviously the more columns that are used, the more certain the identification. Desty and Whyman (368) have reported extensive tables of relative retention volumes (n-pentane = 1) for paraffins, aromatics, cyclopentanes, cyclohexanes, olefins and sulfur compounds on two stationary phases, n-hexatriacontane and benzyldiphenyl.

Multiple Detectors. Detector response is often considered to be the same for all components, or a correction factor is applied (vide infra). On the other hand, the variation in response can be used for identification. Consider two detectors, A and B, which have responses that are different functions of molecular weight. By connecting the two detectors in series at the end of the column, two signals are obtained for each component. One can plot the ratio of detector A response / detector B response versus molecular weight, and then use this curve to estimate the molecular weight of an unknown. Parameters other than molecular weight can be used; for example, the combination of thermal conductivity and radioactivity (579, 660). Perhaps the neatest arrangement of multiple detection is the flame ionization detector from which two independent signals can be obtained - both the flame temperature and an ion current.

Qualitative Identification of Mixtures. In a complicated chromatogram a pattern of peaks (including the peak heights) may help to identify a mixture which is a part of a more complex mixture. An interesting example has been reported by Schuck, Ford and Stephen (639), which in part was concerned with the identification of unburned gasoline in auto exhaust. The extent of the identification is shown in Fig. 13-4. Components present in the fuel were the only ones considered, and then only if they were present in the exhaust at a detectable level. Concentrations of the compounds of interest were then calculated on a molar basis (average of 17 experiments) and normalized for the fuel and the exhaust gas. From the comparison in Fig. 13-4, it is an obvious,

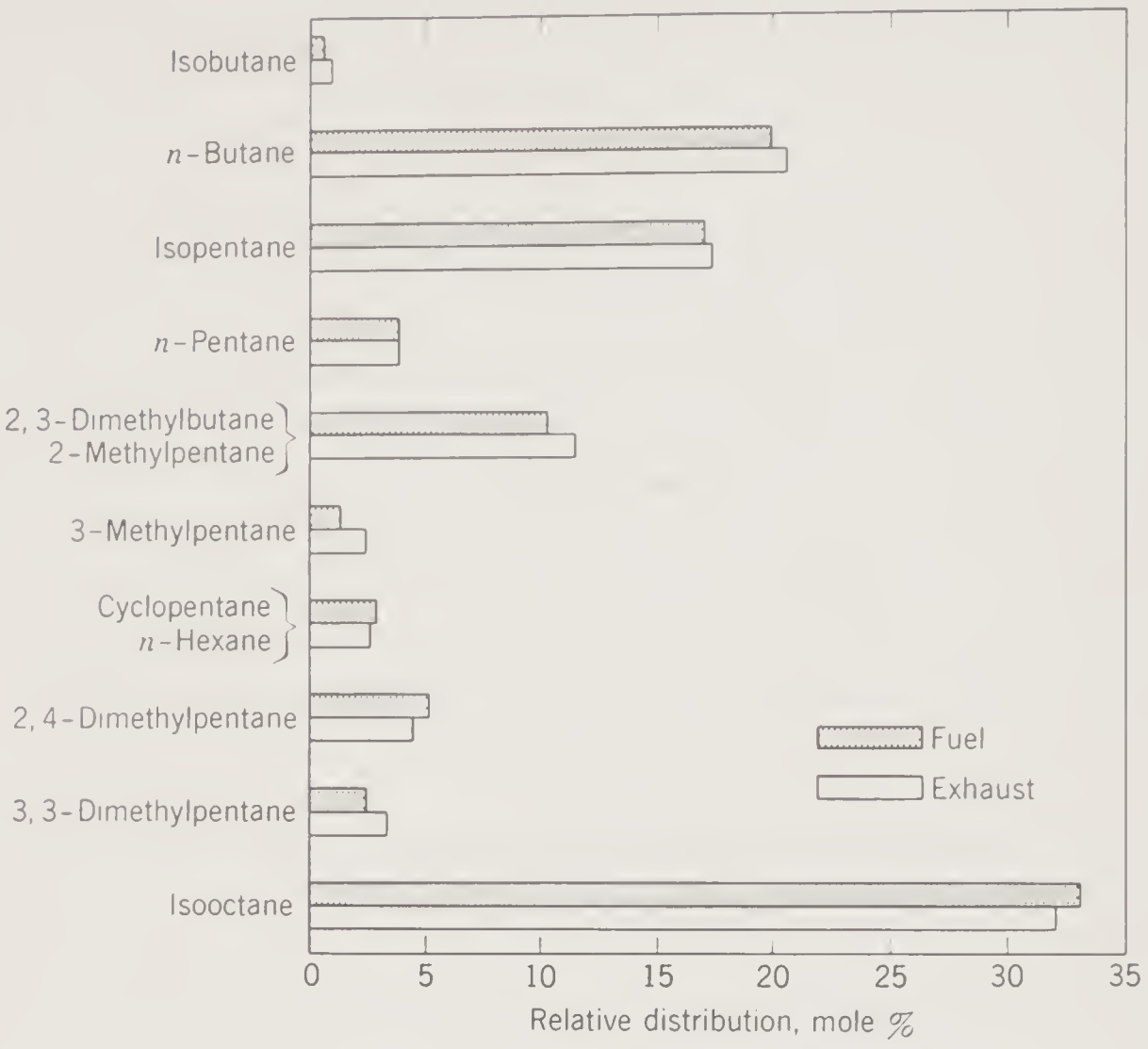

Fig. 13-4. Distribution of certain hydrocarbons in paraffinic fuel and in paraffinic exhaust-air mixtures. Compounds listed = 100%. Courtesy of Air Pollution Foundation (639).

but not necessarily correct, conclusion that there is unburned gasoline in auto exhaust. Some of the discrepancies are beyond experimental error; however, after the cracking process inside the engine, the comparison is surprisingly good.

Identification of Solvent. Just as the retention volumes from an array of solvents can establish the identity of a compound, in the same manner the retention volumes for an array of solutes can identify the solvent. A cleverly composited sample containing a variety of types of components will yield a chromatogram with a peak distribution which is characteristic of the solvent. Mackay (615) has used this technique to identify certain commercial polyoxyethylene derivatives of sorbitan and related compounds using a standard mixture of solutes consisting of esters and alcohols. Such a procedure is obviously cumbersome. How-

ever, with the advent of capillary columns which can be readily coated the method becomes more attractive.

QUANTITATIVE ANALYSIS

Integral Detectors. The response of integral detectors, e.g., gas collected in a buret, volume delivered by an autotitrator, quantity of electricity passed through a coulometer, is a direct measure of the total amount of components which have been eluted from the column. Simple factors converting milliliters of gas, milliliters of titrant, coulombs, etc., to grams of sample are all that is necessary. The remainder of this section is devoted to the interpretation of chromatograms from differential detectors.

Use of Peak Heights. The height of the peak measured from the base line is the simplest method of quantitative analysis. For routine or control analysis where only a few components must be determined, measurements at preset times may supply the necessary information without taking the entire chromatogram. The method is extremely rapid so that it is easy to calibrate the instrument often. If the method is used for process control, a calibration may be programmed after every analysis.

The peak height versus concentration relationship is linear over a limited range of concentration and varies for each component as well as for each column and the operating conditions. Peak heights are most satisfactory for components emerging from the column early where tall, narrow peaks are observed and are less satisfactory for components having long retention times and consequently low, broad peaks. They are advantageous whenever highest accuracy is not essential or is too much of a luxury.

Use of Peak Areas. For a linear chromatographic instrument, the peak area is proportional to the amount of substance present. The proportionality constant depends on the nature of the substance, the type of detector, and whether the amount is expressed on a weight or molar basis. For thermal conductivity detectors, peak areas are also inversely proportional to the flow rate, but are otherwise independent of operating conditions providing only that the detector

temperature is constant. The thermal conductivity detector signal is not a simple function of concentration expressed either in weight per cent or mole per cent. If weight per cent is used, it is possible to obtain accurate results by applying a correction factor which is closely related to the thermal conductivity of the particular component. An extensive study of these factors has been reported by Messner, Rosie and Argabright (686), who found that the relative response (area per mole of component / area per mole of standard substance) of thermal conductivity detectors can be predicted from the molecular weight and class of the compound. They claim that the relative response is independent of the individual sensing unit (filament or thermistor), flow rate, concentration, and detector operating temperature. Extensive tables are given.

For other types of detectors, the response will depend on other factors. The response of the beta-ray detector is primarily a function of weight per cent (hydrogen carrier gas) or molecular weight (argon carrier gas). The gas density balance responds to molecular weight. The introduction of a combustor prior to the detector provides a signal which depends on the molecular composition of the components. The response of the flame temperature detector depends on the heat of combustion.

From the above discussion, it should be clear that indiscriminate use of peak areas as a measure of concentration is subject to serious errors. Calibration and correction factors must be applied according to the expected accuracy of the results.

Internal Normalization of Peak Areas. In this method it is assumed that the total area under a chromatogram represents all of the sample components. The area under each peak is multiplied by the proper correction factor to convert it to grams or moles. The corrected area of a component divided by the total of the corrected areas for all components yields the fraction of each present in the sample. The accuracy of the analysis does not depend on accurate knowledge of the sample size. On the other hand the method does require a complete chromatogram, correction factors and much patience. For rough analysis, the correction factors are often assumed equal to unity with the con-

sequent danger that more credence will be given to the result than it deserves.

If only a few components in the sample are of interest, the method can be abridged using only the area for those components normalized to 1 or 100. In this manner a relative distribution is obtained but not an absolute analysis.

Internal Standardization. In this method a known amount of a standard substance is added to a known volume of sample before it is chromatographed. Thus the concentration of the standard is known. The selection of the standard is important. It should be one that is inert toward all sample components, its peak should be readily and completely resolved from all others, and it should have a retention time intermediate to that of other components. To obtain the concentration of a component it is only necessary to multiply the concentration of the standard by the corrected area for the component and divide by the corrected area for the standard.

The standard substance may be added to the unknown mixture prior to sampling so that the sampling need not be accurate. This method is not limited to peak areas; peak heights may be used as well although calibration factors are imperative.

Measurement of Peak Areas. In many cases, the physical measurement of the peak area is the limiting factor in the accuracy of the results. A number of methods have been proposed.

1. Cut out the peak with a scissors and weigh the paper. This is very inexpensive but tedious. The accuracy is limited by the patience of the operator and the uniformity of the paper.
2. Measure the area with a planimeter. This is a more elegant instrument than a scissors and is relatively inexpensive, but again is limited by the patience of the operator. It is impractical for routine analysis where miles of chart paper may be involved.
3. Multiply the peak height by the peak width at half height. For symmetric peaks this simple method is equally as accurate as the more tedious methods of measuring area. However, peaks with lead-

ing or tailing edges are not suitable.

4. Multiply the peak height by the retention time. The peak width (as well as the width at half height) is directly proportional to retention time and the peak height is inversely proportional to retention time. Therefore, areas determined in this fashion can be treated in the same manner as the actual areas under the peaks.
5. Use an automatic integrator. Several integrators are now available commercially as accessories to standard recorders. (See Chapter 12). The area enclosed by the chromatographic trace is given by a secondary pipping pen or a digital read-out device. Some are designed to record the sub-total area each time the pen returns to the base line, but as yet the problem of overlapping peaks is still left to the operator.

Overlapping Peaks. When either peak areas or peak heights are used, difficulties arise if the components are not completely separated, resulting in overlapping peaks. If accurate results are required, it may be well to look for another stationary phase with a greater resolving power or to collect the unresolved material for further treatment.

Brace (671) has made an interesting study of the quantitative evaluation of overlapping peaks. He used an ingenious simplification which, however, is valid for other cases. The sample was a blend of benzene, toluene and p-xylene in a ratio of 2:3:5 - chosen because all peaks were approximately the same height. A conventional analysis gave three completely resolved peaks. Incomplete resolution was simulated by the successive addition of two samples with a variable time delay between injections. Thus two adjacent peaks were obtained for each of the three components. The degree of resolution between any two peaks for the same component was increased by increasing the time delay. Peak heights were varied by changing the ratio of the sample sizes. Peak widths were changed by varying the flow rate and temperature.

In all cases the two benzene peaks were well resolved permitting a determination of the peak ratios that should be obtained for the partially resolved p-xylene peaks.

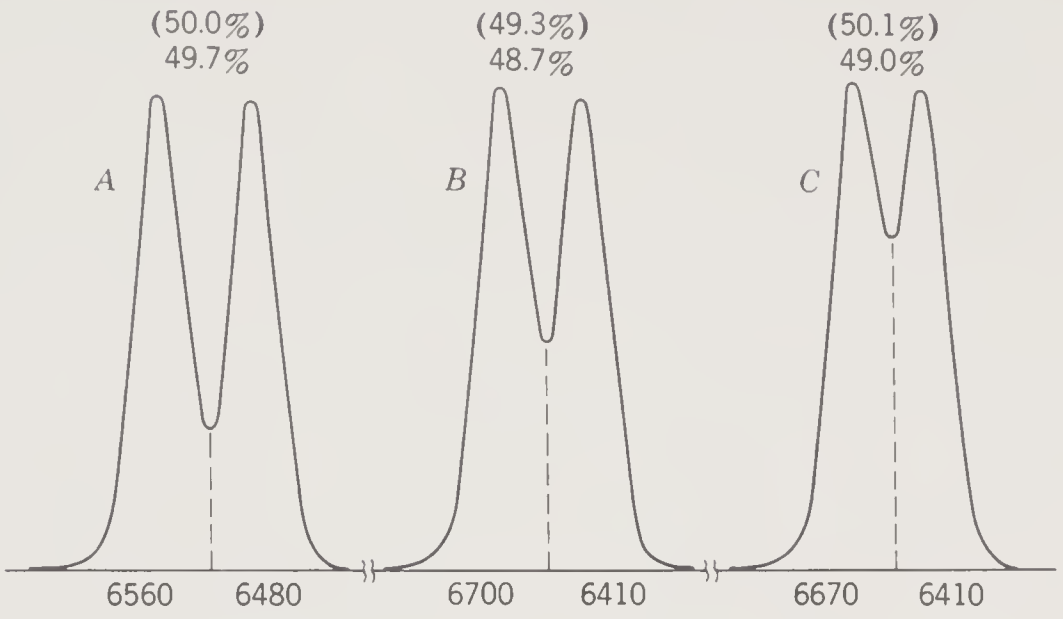

Fig. 13-5. Incomplete resolution of peaks with similar peak heights. After Brace (671).

All data given refer to the latter peaks. Areas were measured with an integrator attachment made by the Disc Instrument Company.

Fig. 13-5 shows three degrees of non-resolution. Below each pair of peaks is the integrated area using the minimum between the peaks as a dividing line. The values above the peaks are the peak ratios (area of the peak / total area of both peaks) using the integrated values. In parenthe-

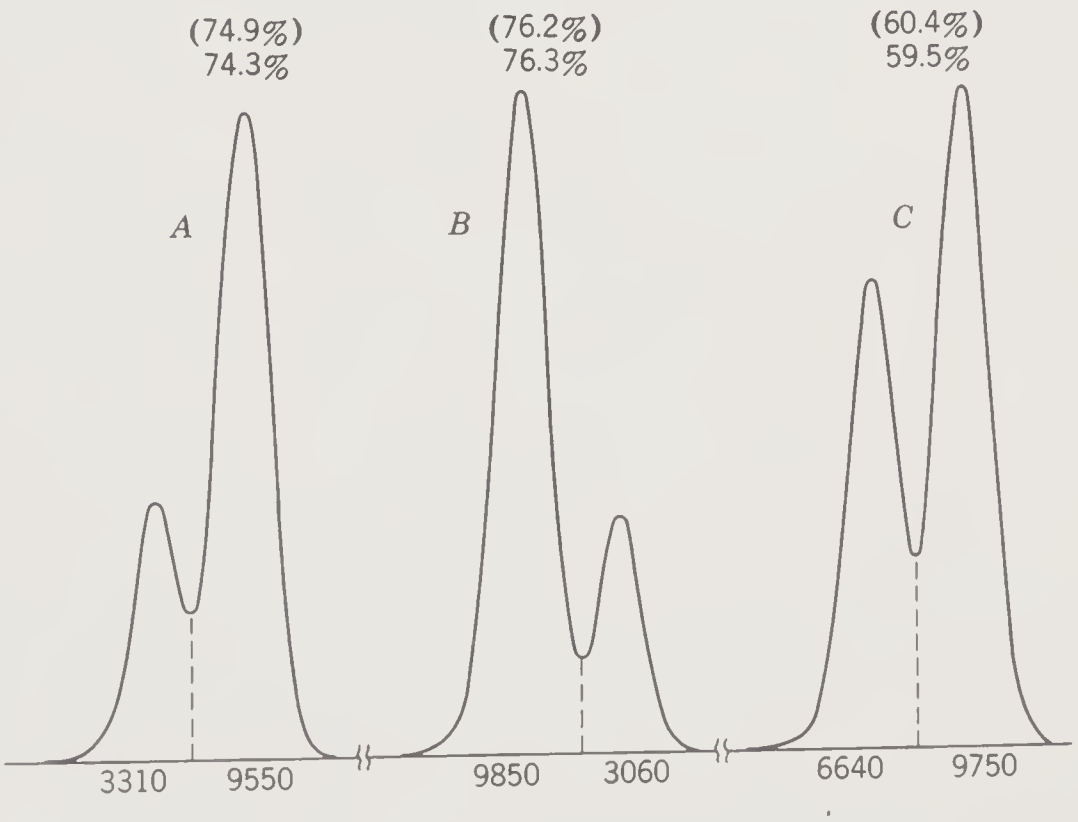

Fig. 13-6. Incomplete resolution of peaks with different peak heights. After Brace (671).

ses is the corresponding value determined from the completely resolved benzene peaks.

Fig. 13-6 shows the effect of different peak heights produced by using two different sample sizes. The peak ratios have been determined as above, and again show adequate agreement.

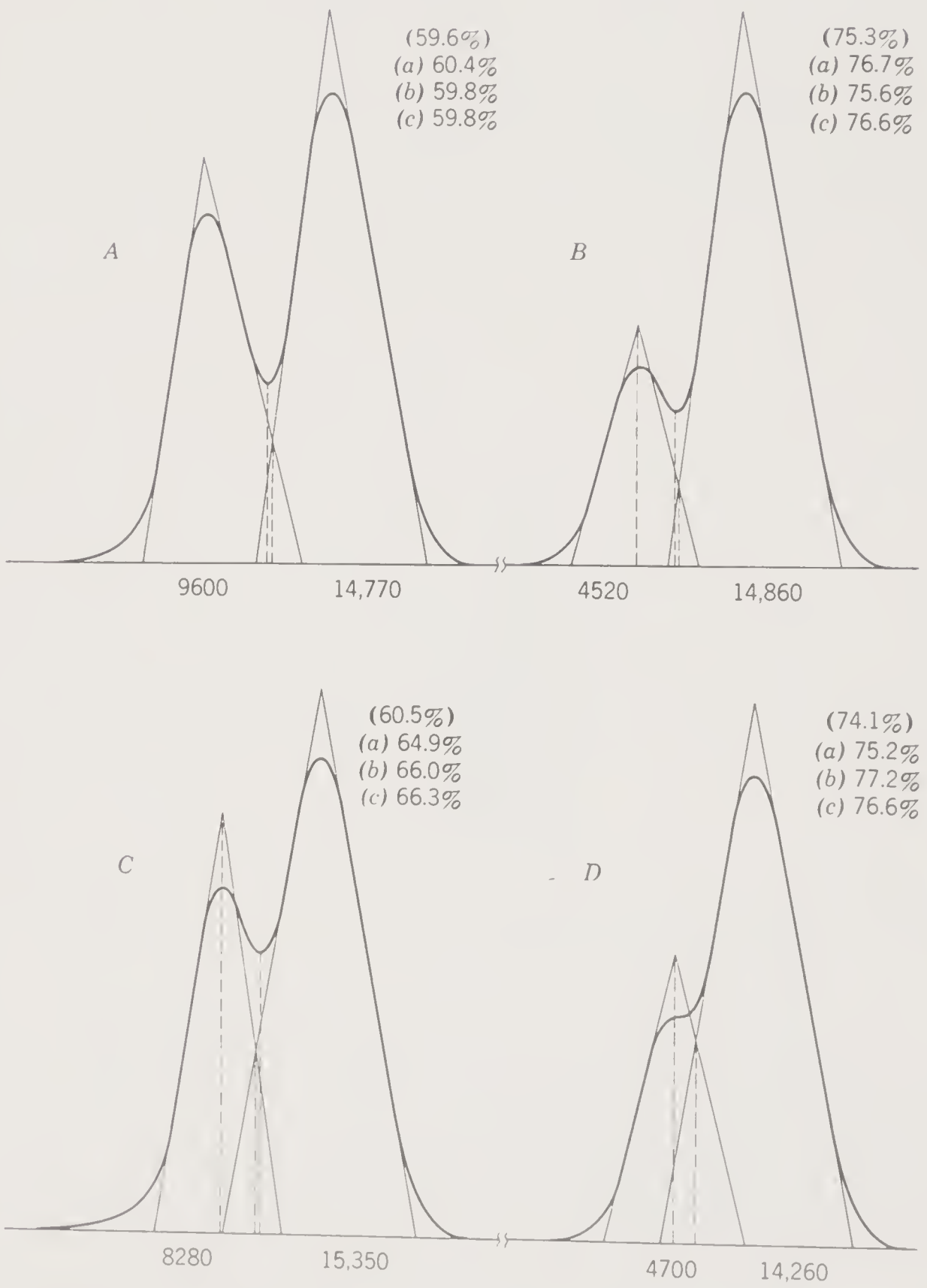

Fig. 13-7. Incomplete resolution of peaks of different heights and widths. After Brace (671).

Broader peaks, simulated by changing the flow rate and temperature, result in still poorer resolution as shown in Fig. 13-7. Here the major peak in each pair has been evaluated by four techniques. The value in parentheses has been determined from the ratio of the benzene peaks and is assumed to be the correct value. The (a) value above each major peak was determined directly from the integrated values using the minimum between the peaks as a dividing line. The (b) value was determined from the "corrected" integrated values using as a dividing line the perpendicular dropped from the intersection of the tangents to the inside slopes of the overlapping peaks. The (c) value was obtained by approximating triangles as explained in Fig. 13-8.

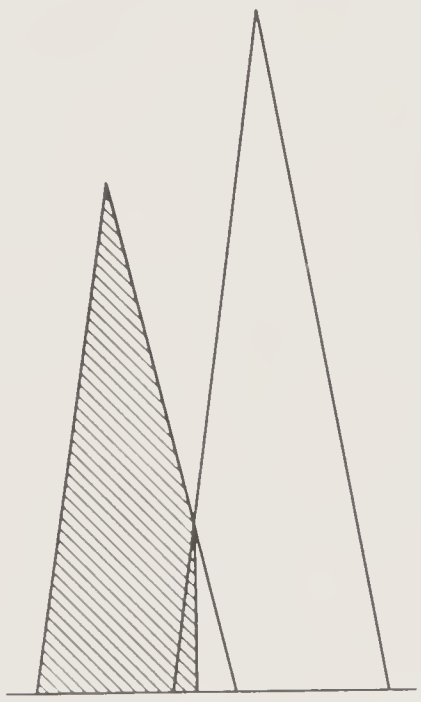

Fig. 13-8. Resolution by method of approximating triangles. After Brace (671).

When non-resolution obviously distorts one of the inside slopes as in Fig. 13-7, B and C, the inside tangent would be completely misleading. The procedure then is to pass a perpendicular through the peak maximum and construct an isosceles triangle using the outside tangent as one side.

The example shown in Fig. 13-7 D is an extreme case of non-resolution and illustrates roughly the limitations of these techniques.

The method of approximating triangles can be applied whether or not there is peak overlap. Triangles are

formed from the tangents or hypothetical tangents as shown in Fig. 13-8. The area corresponding to the first peak is shaded and the remaining area corresponds to the second peak. Each area divided by the total area gives the per cent composition. The total area enclosed by the triangles tends to be higher than that obtained from integration. From the limited amount of data available, the correction seems to be consistent and is of no concern if all data is obtained in the same manner.

Brace concludes that "the results of this investigation suggest that resolution must be very poor indeed in order to interfere seriously with quantitative results by gas chromatography."

From this limited study, we cannot conclude that this technique will give equally satisfactory results in all cases. An extreme case is shown in Fig. 13-9, where the peak of a trace amount (0.2%) of sec-butyl alcohol is masked by the trailing edge of the major component, isopropyl alcohol. The peak height is not a suitable measure of concentration, and the peak area is evidently determined by using an artificial base line drawn by continuing the isopropyl alcohol trace in a smooth curve. This technique was checked with known synthetic mixtures (439). A definitive study of the quantitative interpretation of overlapping peaks would be very valuable if general methods can be proved valid.

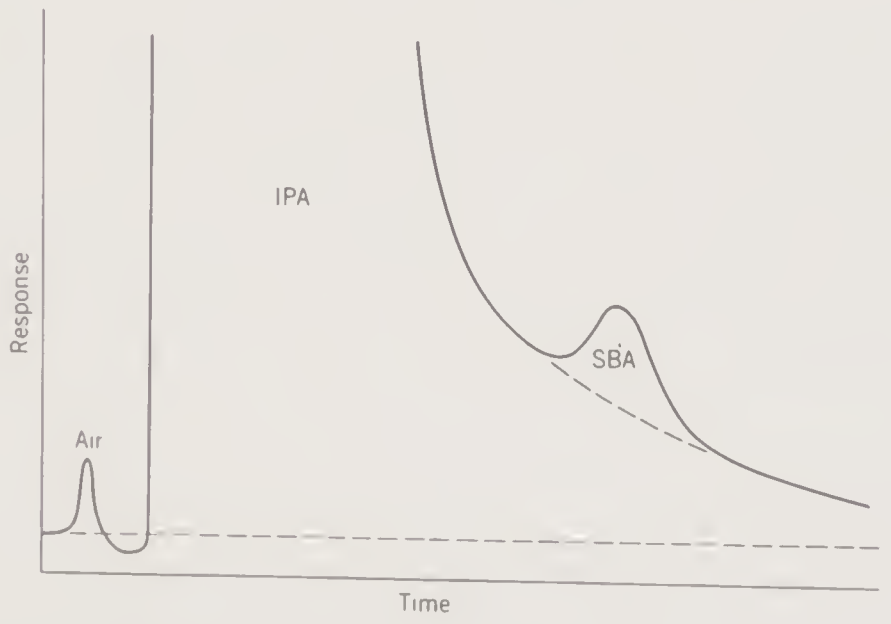

Fig. 13-9. Trace amount of secondary butyl alcohol (SBA) in crude isopropyl alcohol (IPA). Courtesy of Reinhold Publishing Corporation (439).

Quantitative Analysis of the Solvent. At a fixed temperature and sample size, the retention time of a solute is proportional to the weight of the solvent in the stationary phase. Retention times, therefore, give some quantitative information regarding the solvent.

Use of retention times to analyze a binary solvent mixture is purely speculative at this stage, but with the field moving so fast, what is speculation today may be an accomplished fact tomorrow. Consider the following rather useless example to illustrate the point. Acetone is much more soluble in water than in glycerol, and there is little doubt that the retention time of acetone would be greater for a water stationary phase than for glycerol. It seems intuitively obvious that for a fixed weight of mixed solvent (water plus glycerol) the retention time of acetone should increase in a regular fashion as the ratio of water to glycerol is increased. Using two solutes, such as acetone and diethyl ketone, it is probable that the ratio of retention times would be a unique function of the composition of the liquid phase at a given temperature. The retention time ratio has the obvious advantage that it does not depend on the manner of packing the column or other operational parameters.

Another case of perhaps greater interest is the estimation of relative amounts of optical isomers. It will be recalled that optical isomers are identical in all physical properties for all operations that are symmetric. The physical properties can be different, and appreciably so, for unsymmetric operations. Two optical isomers could conceivably be separated if they were sufficiently volatile, and if the stationary phase was optically active or contained an optically active substance. Conversely, a single member of an optically active pair should have a retention time that depended on the relative amounts of optical isomers comprising the solvent.

Appendix I

LIST OF MANUFACTURERS

A. MANUFACTURERS OF GAS CHROMATOGRAPHS

American Instrument Company, 8030 Georgia Ave., Silver Spring, Maryland
Barber-Colman Company, Rockford, Illinois
Beckman, Scientific Instruments, Fullerton, California
Burrell Corporation, 2223 Fifth Ave., Pittsburgh 19, Pennsylvania
Central Scientific Company, 1700 Irving Park Blvd., Chicago, Illinois
Consolidated Electrodynamics Corporation, 300 North Sierra Madre Villa, Pasadena, California
Davis Instruments, 47 Halleck St., Newark 4, New Jersey
F and M Scientific Corporation, 1001 Kendall Rd., Wilmington 5, Delaware
Fisher Scientific Company, 711 Forbes Ave., Pittsburgh 19, Pennsylvania
Jarrell-Ash Company, 26 Farwell St., Newtonville 60, Massachusetts
Leeds and Northrup, 4907 Stenton Ave., Philadelphia 44, Pennsylvania
Loe Engineering Company, 237 North Fair Oaks Ave., Pasadena, California
Perkin-Elmer Corporation, Norwalk, Connecticut
Podbielniak, Incorporated, 341 East Ohio St., Chicago 11, Illinois

Precision Scientific Company, 3737 West Cortland St., Chicago 47, Illinois
Research Specialties Company, 200 South Garrard Blvd., Richmond, California
Wilkens Instrument and Research, Incorporated, P.O. Box 313, Walnut Creek, California

B. OTHER COMPANIES MENTIONED IN TEXT

Barnes Engineering Company, 30 Commerce Rd., Stamford, Connecticut
Conoflow Corporation, 2012 Arch St., Philadelphia, Pennsylvania
Disc Instrument Company, 12671 Bubbling Well Rd., Santa Ana, California
Fischer and Porter Company, Hatboro, Pennsylvania
Gow-Mac Instrument Company, 100 Kings Rd., Madison, New Jersey
Johns-Manville Corporation, 22 East 40th St., New York 16, New York
Hamilton Company, 1134 Whitley St., Whittier, California
Hoke, Incorporated, 138 South Dean St., Englewood, New Jersey
Linde Air Products Company, 30 East 42nd St., New York 17, New York
Victory Engineering Company, Springfield Rd., Union, New Jersey

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